

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

CM 1741 M

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09B 62/02, 62/503, 62/20, 62/04	A1	(11) International Publication Number: WO 99/51686 (43) International Publication Date: 14 October 1999 (14.10.99)
(21) International Application Number: PCT/US99/07294 (22) International Filing Date: 1 April 1999 (01.04.99) (30) Priority Data: PCT/US98/06541 2 April 1998 (02.04.98) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BROCK, Earl, David [US/US]; 7395 Wethersfield Drive, West Chester, OH 45069 (US). LEWIS, David, Malcolm [GB/GB]; 13 St. Richard Road, Otley, West Yorkshire LS21 2AL (GB). YOUSAF, Taher, Iqbal [GB/GB]; 10 School Lane, Egham, Surrey TW20 9LQ (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).	(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: REACTIVE DYE COMPOUNDS (57) Abstract Reactive dye having a Fixation Value (F) on cellulosic substrates of 95 % or greater as measured by the Fixation Value Technical Test Method (at 2:1 standard depth). In addition, the compounds herein have high Exhaustion Values (E), high Efficiency Values (T) and show significant improvements in terms of reducing spent dyestuff in effluent, increasing dye affinity to the substrate, increasing the dye-substrate covalent bonding, increasing the ability to dye substrates at room temperature, decreasing the amount of dye that is removed during the post dyeing "soaping off process" and therefore simplifying the post dyeing "soaping off process" traditionally associated with dyeing cotton with fibre reactive dyes and reduction of staining of adjacent white fabrics. In addition, the compounds prepared above provide more intense dyeings and require less levels of salt for dyeing cotton substrates.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Reactive Dye Compounds

Technical Field

The present invention relates to reactive dye compounds. In particular the present invention relates to reactive dye compounds having improved dye-bath Exhaustion (E) and improved dye-fibre covalent Fixation (F).

5

Background of the Invention

Reactive dye compounds are known in the art for dyeing various substrates. Such substrates include for example proteinaceous materials such as keratin, e.g. found in hair, skin and nails and various animal body parts such as horns, hooves and feathers, and other naturally occurring protein containing materials, e.g. silk and saccharide-derived materials such as those derived from cellulose or cellulose derivatives, e.g. natural products such as cotton, and synthetic fibres such as polyamides.

Examples of classes of such reactive dyes which are well known in the art include dyes containing a mono- or dichloro- or fluoro- 1,3,5-triazinyl group, mono- or dichloro or fluoro-pyrimidyl group, beta-halogen-propionyl group, beta-halogenoethyl-sulphonyl group, beta-halogenoethylsulphamyl group, chloroacetyl amino, beta-(chloro-methyl)-beta-sulphatoethylsulphamyl group, or a vinyl sulphonyl group.

In the case of the dyes containing a triazinyl group or a pyrimidyl group, in place of the reactive halogen atoms one can use other groups which dissociate in the presence of alkali. Canadian Patent 771632, for example, discloses examples of such other groups including sulphonic acid, thiocyanate, sulphophenoxy, sulphophenyl thio, nitrosulphophenoxy groups, and quaternary ammonium groups.

25

Dyes and Pigments 14, 1990, pages 239-263, "Synthesis and Application of Reactive Dyes with Heterocyclic Reactive Systems" discloses fibre reactive dyes containing monochloro- or dichloro-pyrimidine heterocycle with quaternary ammonium substituents.

30

There are many different types of commercially-available reactive dyes for dyeing cellulosic and polyamide-type substrates. However, a critical problem still facing the textile dye industry today is the significant level of dyestuff material which remains in the effluent waste water after the dyeing process is finished. The industry measure for this problem is known as dye-bath Exhaustion (E). A high Exhaustion value for a particular dye compound means that a low level of spent dye remains in the effluent after the dyeing process is complete, while a low Exhaustion value means that a high level of spent dye remains in the effluent. There is clearly a need therefore for new dye compounds which have higher Exhaustion Values compared with commercially available dye compounds, and which provide benefits in terms of reducing levels of spent dyestuff in effluent water.

As well as having a high Exhaustion Value, it is also important for a dye compound to have a high dye-fibre covalent Fixation Value (F). The Fixation Value (F) of a dye compound is a measure of the dye affinity at the substrate surface. Thus, there is clearly a need to provide dye compounds having increased Fixation Values. A high Fixation Value can result in a simplification of the post dyeing "soaping off process" traditionally associated with fiber reactive dye compounds. In particular, a high Fixation Value can result in a reduced time spent on the "soaping off process" together with a reduced cost.

It has now been surprisingly found that a new class of fibre reactive dye compounds comprising a nitrogen-containing heterocycle such as pyrimidine substituted with at least one quaternized nitrogen derivative such as nicotinate, exhibit significantly increased values of Exhaustion (E) and Fixation (F). These dyes can be used on a wide variety of substrates. They are particularly useful for cellulosic substrates, such as cotton, and show significant improvements in terms of reducing spent dyestuff in effluent, increasing dye affinity to the substrate, and simplifying the post dyeing "soaping off process" traditionally associated with reactive dyes. In addition, the compounds of the present invention provide significantly more intense dyeings, and can be used for both high and low temperature dyeing, hence reducing the cost of the dyeing process. Furthermore, the compounds of the present invention can be used together with specific chromophores for cellulose substrate dyeing leading to significantly reduced levels of salt needed for dyeing.

Summary of the Invention

According to the present invention there is provided a reactive dye compound having a Fixation Value (F) on cellulosic substrates of 95% or greater as measured by the
5 Fixation Value Technical Test Method (at 2:1 standard depth).

The compounds of the present invention exhibit increased Exhaustion (E) and Fixation (F) values and provide improvements in terms of reducing spent dyestuff in effluent, increasing dye affinity to the substrate, simplifying the post dyeing "soaping off
10 process" traditionally associated with fiber reactive dyes and ability to dye at room temperature and elevated temperatures. In addition, the compounds of the present invention provide significantly more intense dyeings, i.e. greater colour intensity in the dyed substrate.

Detailed Description of the Invention

As used herein the term "reactive dye" means a dye containing one or more reactive groups, that is to say one or more groups capable of forming covalent bonds with the substrate to be dyed, or a dye which forms such a group in situ.
15

As used herein the term "Exhaustion" in relation to reactive dyes means the percentage of dye which is transferred from a solution of the dye to the substrate to be treated at the end of the dyeing process, before rinsing and soaping. Thus 100% Exhaustion means that 100% of the dye is transferred from the dye solution to the substrate.
20

As used herein the term "Fixation" in relation to reactive dyes means the percentage of dye which covalently bonds with the substrate, based on the dye originally absorbed during the dyeing process. Thus 100% Fixation means that 100% of the dye absorbed is covalently bonded with the substrate.
25

The reactive dye compounds of the present invention have a Fixation Value (F) on cellulosic substrates of 95% or greater as measured by the Fixation Value Technical Test Method described hereinbelow (at 2:1 standard depth). Preferably the reactive dye compounds of the present invention have a Fixation Value on cellulosic substrates of
30 97% or greater, more preferably 99% or greater.
35

Preferred reactive dye compounds herein have an Exhaustion Value (E) on cellulosic substrates of 90% or greater as measured by the Exhaustion Value Technical Test Method described hereinbelow (at 2:1 standard depth). Preferably the reactive dye compounds of the present invention have an Exhaustion Value of 93% or greater, more preferably 95% or greater, even more preferably 97% or greater, especially 99% or greater.

The total efficiency of reactive dyes can be measured by their Efficiency Value (T) which can be calculated from the Exhaustion Value (E) and Fixation Value (F) using the following equation:

$$\%T = (F \times E) / 100$$

Thus according to another aspect of the present invention there is provided reactive dye compounds having an Efficiency Value (T) on cellulosic substrates of about 86.5% or greater, preferably about 90% or greater (at 2:1 standard depth), more preferably about 93% or greater, even more preferably about 95% or greater, even more preferably about 97% or greater, especially about 99% or greater.

Exhaustion Value Technical Test Method

Theory

For dyeing 100g of cotton, typically 1% dye on mass of fibre (o.m.f.) is applied from a long liquor dye bath (typically 10 parts water to 1 part cotton). The dye is absorbed by the fibre and then covalently bonds to the cotton fibre and is said to "exhaust" onto the fibre. This phenomenon is commonly called the percentage Exhaustion Value (%E). Thus a dye which produces a water white dye bath on dyeing, i.e. a dye bath wherein all the dye in the dye bath is taken up by the fibre, would have a %E Value of 100%. The concentration of dye in the dyebath, initially (at time = 0) and at the end of the dyeing process, may be measured directly by using absorbance (Optical Density (OD)) measurements of dye bath samples (at the wavelength of maximum absorbance of the dye).

The %E Value can be calculated using the following equation:

$$E\% = (b-a)/b \times 100$$

-Equation 1

where b is the initial Optical Density of the dye bath at the start of the long liquor dyeing process (at time = 0) and where a is the final Optical Density of the dye bath at the end of the long liquor dyeing process.

Instruments Needed

UV/Visible Scanning Spectrophotometer - to obtain maximum accuracy of measurement it is necessary to dilute the liquor so that a sample gives an Optical Density of below 0.6 (for adherence to Beer's Law).

Test Procedure

1. The following two dye baths were prepared to obtain a 2% on mass of fibre (o.m.f.) depth of shade:

Dye Bath A

2g of dye was dissolved in 48g of water. 8g of sodium sulfate was dissolved in 42g of water. The two solutions were mixed to form dye bath A.

Dye bath B

A second dye bath B was prepared in the same way as for dye bath A.

2. 100g of bleached woven cotton fibre was added to Bath A.

3. Bath A is agitated at 23C for 30 minutes. 2g of trisodium phosphate is then added to adjust the pH of bath A to pH 11.25 and dyeing is continued for a further 30 minutes at the end of which dyeing is complete.

4. On completion of the dyeing process the Optical Density of Dye Bath A is measured using a Kontron UV/Visible Spectrophotometer to give the value "a" in equation 1.

5. The Optical Density of Dye Bath of B was measured on the same instrument to obtain the value "b" in equation 1.

Fixation Value Technical Test Method

5

Test Procedure

1. The dyed fabric obtained at the end of the long liquor dyeing process in the Exhaustion Value Technical Test Method is removed and excess liquor is squeezed into the dye bath.
2. The fabric is cut into two equal weight parts : Sample A and Sample B
3. Sample B is dried in air overnight and kept as a control. Sample A is boiled for 30 minutes in 100ml of an aqueous solution of Sandozin NIE (non-ionic ethoxylated fatty alcohol detergent commercially available from Clariant) (2g/litre) in a 500ml beaker. The procedure is repeated until the extract solution is visually colourless. Sample A is then dried by hanging in air overnight.
4. The reflectance spectra of both Samples A and B are measured using a Macbeth Colour Eye reflectance spectroscope with the following conditions:
- Primary illuminant D65
 - Secondary illuminant C
 - Specular component excluded
 - UV excluded
 - Small aperture
 - 10° Observer
5. The reflectance values for Samples A and B can be used to obtain their K/S (Fixation) Values - see equation 3 below. The K/S or Kulbelka Munk Values are proportional to the amount of dye remaining on the samples.

Theory

35

The percentage relative Fixation (F%) or the amount of dye absorbed by the fibre which is covalently fixed is defined by the following equation:

$$\%F = \frac{K/S_A}{K/S_B} \times 100 \quad \text{-Equation 2}$$

K/S (Fixation) Values can be calculated from reflectance data using the following equation:

$$\frac{(1-R\lambda)^2}{2R\lambda} = \frac{K}{S\lambda} \quad \text{-Equation 3}$$

where $\frac{K}{S\lambda}$ = K/S of the sample at wavelength λ

$R\lambda$ = fractional reflectance at wavelength λ

K/S is derived from the Kubelka Munk theory and can be used as a measure of the amount of dye on the fibre. The higher the K/S Value the more dye on the fibre.

Thus for Sample A, Fixation Value = K/S_A , and for Sample B, Fixation Value = K/S_B .

The percentage relative Fixation or the amount of dye absorbed by the fibre which is covalently fixed is thus defined as :

$$\%F = \frac{K/S_A}{K/S_B} \times 100 \quad \text{-Equation 2}$$

The total overall efficiency of the process i.e. the fraction of dye originally applied which ends up covalently fixed to the fibre) may then be calculated as follows:

$$\%T = \frac{F \times E}{100} \quad \text{-Equation 4}$$

Preferred compounds of the present invention comprise a chromophore moiety and a nitrogen-containing heterocycle linked via a linking group. The nitrogen-containing heterocycle preferably has at least one quaternized nitrogen derivative.

5 Chromophore Moiety

The reactive dye compounds herein can comprise one or more chromophore moieties. In reactive dye compounds comprising two or more chromophore moieties these can be the same or different. Preferably the reactive dye compounds herein comprise from one
10 to three chromophore moieties.

Any chromophore moieties suitable for use for dyeing substrates can be used in the present invention. The term chromophore as used herein means any photoactive compound and includes any coloured or non-coloured light absorbing species, eg.
15 fluorescent brighteners, UV absorbers, IR absorbing dyes.

Suitable chromophore moieties for use in the dye compounds herein include the radicals of monoazo, disazo or polyazo dyes or of heavy metal complex azo dye derived therefrom or of an anthraquinone, phthalocyanine, formazan, azomethine, dioxazine,
20 phenazine, stilbene, triphenylmethane, xanthene, thioxanthene, nitroaryl, naphthoquinone, pyrenequinone or perylenetetracarbinide dye.

Suitable chromophore moieties for use in the dye compounds herein include those disclosed in EP-A-0,735,107 (Ciba-Geigy), incorporated herein by reference, including
25 the radicals described therein which contain substituents customary for organic dyes, such as sulphonate substituents which enhance the water-soluble properties of the dye compound.

Most preferred chromophore D groups for use herein are polysulphonated azo
30 chromophores such as those present in Procion (RTM) dyes commercially available from BASF, Drimalan (RTM) dyes commercially available from Clariant, Drimarene (RTM) dyes commercially available from Clariant and Levafix (RTM) commercially available from Dystar.

35 Nitrogen-containing heterocycle

The reactive dyes of the present invention comprise at least one nitrogen containing heterocyclic moiety. In reactive dye compounds containing two or more nitrogen containing heterocycles these can be the same or different. Preferably the reactive dye compounds herein comprise from one to three nitrogen containing heterocycles. At least one of the nitrogen containing heterocycle moieties herein is substituted with at least one thio-derivative and at least one quaternized nitrogen derivative.

Suitable nitrogen containing heterocycles for use herein include monocyclic, bicyclic or polycyclic, unsaturated heterocycles containing at least one nitrogen heteroatom. When monocyclic rings are used, they are preferably selected from unsaturated rings having from about 3 to about 7 ring atoms, especially 5 or 6 ring atoms, comprising from about 1 to about 3 nitrogen heteroatoms, preferably 2 or 3 nitrogen heteroatoms. When bicyclic heterocycles are used, they preferably comprise an unsaturated nitrogen containing heterocycle having 3 to 7 ring atoms, preferably an unsaturated nitrogen containing heterocycle having 5 or 6 ring atoms comprising 1 or 2 nitrogen atoms, fused to a 5 to 7 membered carbocycle preferably a 6-membered unsaturated carbocycle. When bicyclic heterocycles are used, the thio- and quaternized nitrogen substituents are preferably attached to the nitrogen containing heterocyclic ring.

Preferred for use herein are 5 or 6 membered unsaturated nitrogen containing monocyclic heterocyclic rings comprising 2 or 3 nitrogen heteroatoms or bicyclic rings containing a 5 or 6 membered unsaturated heterocyclic ring containing 2 nitrogen heteroatom fused to a 6 membered unsaturated carbocycle.

Examples of suitable heterocycles for use herein include, but are not necessarily limited to triazine, pyrimidine, quinoxaline, pyrimidinone, phthalazine, pyridazone and pyrazine.

Preferred for use in the compounds herein are triazine, pyrimidine and quinoxaline.

Linking Moiety

The compounds herein further comprise a linking moiety to link each nitrogen-containing heterocycle to each chromophore moiety. Any linking moieties suitable for use in dyeing substrates can be used in the present invention. Preferably the linking moiety is selected from NR, NRC=O, C(O)NR, NRSO₂ and -SO₂NR wherein R is H or

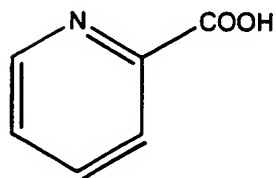
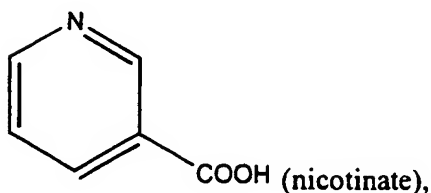
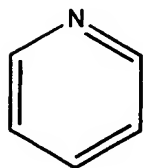
C₁-C₄ alkyl which can be substituted by halogen, preferably fluorine or chlorine, hydroxyl, cyano, C₁-C₄ alkoxy, C₂-C₅ alkoxycarbonyl, carboxyl, sulfamoyl, sulfo or sulfato. When the heterocycle is a triazine or pyrimidine a preferred linking moiety is NR, preferably where R is H or C₁-C₄ alkyl, more preferably where R is H or CH₃, especially H. When the heterocycle is quinoxaline or phthalazine, a preferred linking moiety is NRC=O, where R is H or C₁-C₄ alkyl, more preferably where R is H or CH₃, especially H.

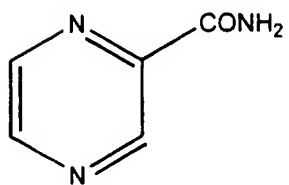
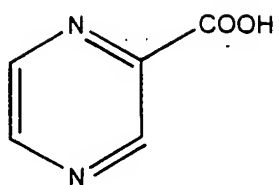
A preferred substituent of the compounds herein is a quaternized nitrogen substituent.

Suitable quaternized nitrogen derivatives for use herein can be represented by Q⁺ wherein Q is selected from amines, saturated or unsaturated, substituted or unsubstituted nitrogen containing heterocycles having from about 3 to about 8 ring members and comprising at least one nitrogen heteroatom.

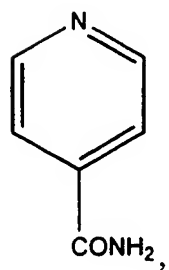
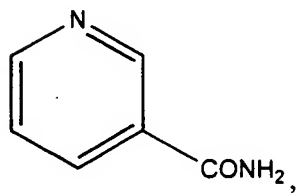
Particularly preferred for use herein are Q groups selected from:

NR³,

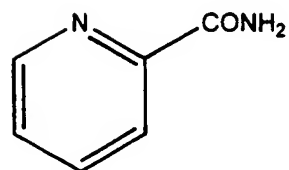




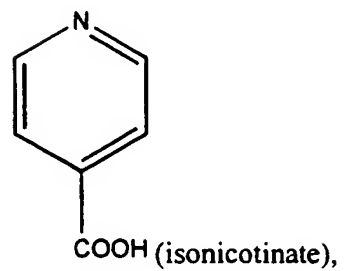
5

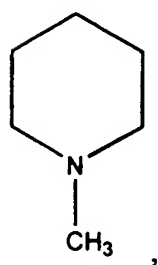
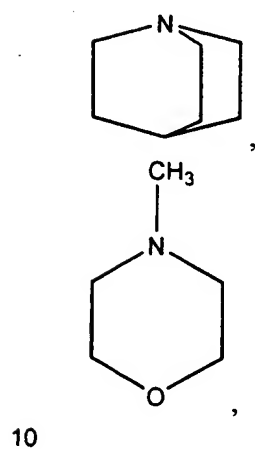
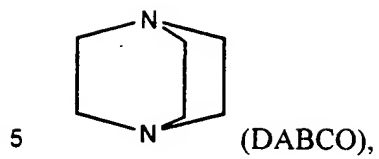
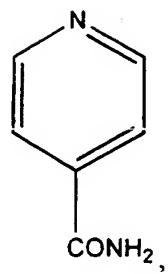


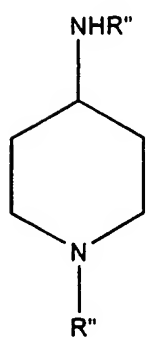
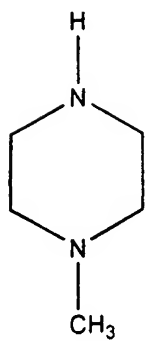
10



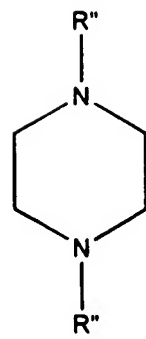
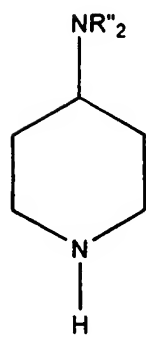
15



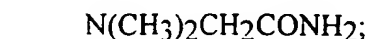
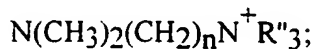
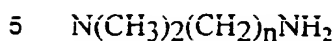
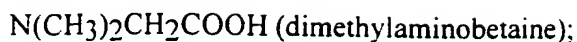
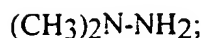




5



10



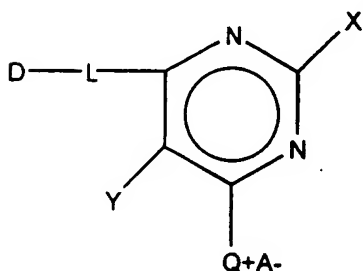
wherein R'' is C₁-C₄ alkyl and n is an integer of from 1 to 4.

Particularly preferred quaternized nitrogen derivatives for use herein are nicotinate, DABCO, dimethylaminobetaine and isonicotinate, especially nicotinate.

15

The quaternized nitrogen derivative is attached to the nitrogen-containing heterocycle via its tertiary nitrogen atom.

20 In the case where the nitrogen containing heterocycle is a pyrimidine ring, preferred reactive dye compounds comprising at least one quaternized nitrogen derivative can be represented by the formula (I):



25

wherein: D is a chromophore group as defined hereinabove;

L is a linking moiety as defined herein above;

30

Q is a quaternized nitrogen derivative as defined hereinabove;

X and Y are independently selected from chlorine, bromine, fluorine or hydrogen;

35

A is selected from halogen, preferably chlorine or fluorine;

provided that at least one of X and Y is fluorine.

and salts and esters thereof.

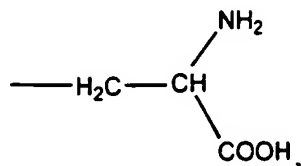
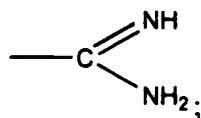
In preferred embodiments, X is selected from chlorine or hydrogen, especially chlorine and Y is fluorine.

5

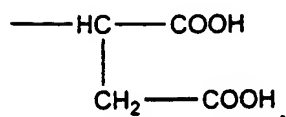
Another preferred substituent on the heterocyclic ring in addition to the quaternized nitrogen derivative is a thio-derivative. Suitable thio-derivatives for use herein include, but are not necessarily limited to groups having the formula SR' wherein R' is selected from H or alkyl or preferably short chain alkyl (preferably less than about 6 carbon atoms), alkanol, alkyl carboxylate, alkylamide, alkylsulphonate, alkyl phosphonate, 10 alkyl thiosulphonate, alkylamine, alkyl thiosulphate, aryl sulphonate, aryl carboxylate, aryl phosphate, aryl amine, cyanates, sulphonates, branched alkyl thio carboxylates, branched alkanol thiols, guanides, alkyl- α -amino- α -carboxylate, (di) thio alkyl esters of glycerol, alkyl thiol alkyl esters of glycerol, alkyl esters, mono thio diesters, thiol alkyl 15 esters of ethylene glycol, alkyl thiol alkyl ester of ethylene glycol and alkyl thiolipoates. Preferably R' is selected from alkyl carboxylates and alkanols.

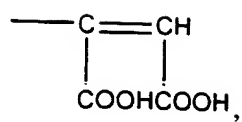
Examples of suitable thio-derivatives include SR' groups where R' is C₁-C₄ alkyl, (CH₂)_nCOOH, (CH₂)_nCONH₂, (CH₂)_nSO₃H, (CH₂)_nCOOM, (CH₂)_nPO₃H, 20 (CH₂)_nOH, (CH₂)_nSSO₃⁻, (CH₂)_nNR["]₂, (CH₂)_nN⁺R["]₃, PhSSO₃⁻, PhSO₃H, PhPO₃H, PhNR["]₂, PhN⁺R["]₃, -CN, SO₃⁻, (CH₂)₂CH(SH)R["](CH₂)₃COOH, -CH₂CHOHCH₂SH, and

25

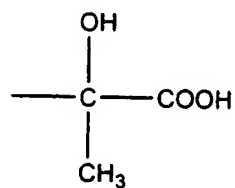
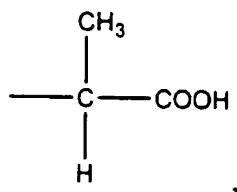


30

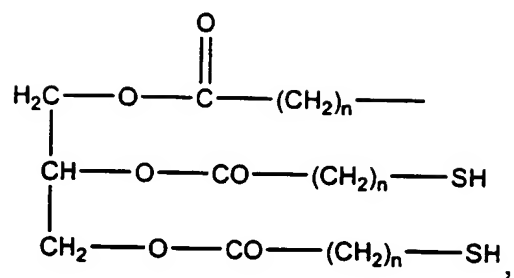




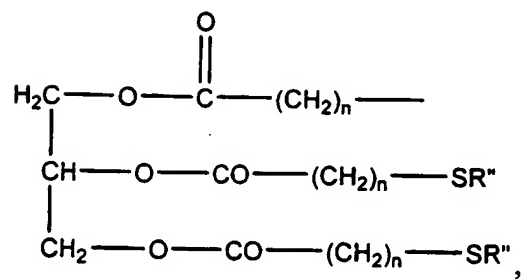
5



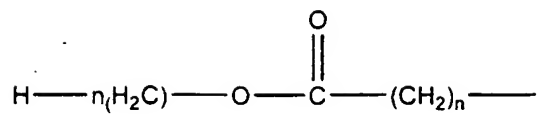
10



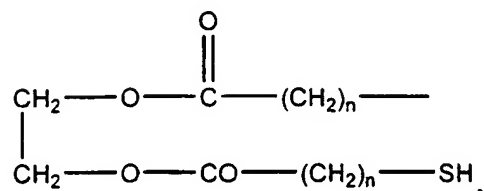
15



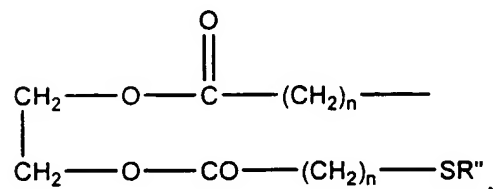
20



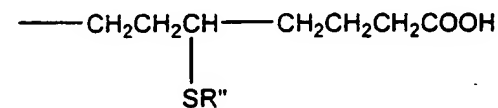
5



10



15



n is an integer in the range of 1 to 4 wherein within the same molecule n is not necessarily the same integer; and M is a cation of alkaline earth metal, alkali metal, NH_4^+ or NR''^3_+ .

20 Preferred thio-derivatives for use herein have the formula SR' wherein R' is $(\text{CH}_2)_n\text{COOH}$, $(\text{CH}_2)_n\text{OH}$, and $(\text{COOH})\text{CH}_2\text{CH}_2(\text{COOH})$, wherein n is an integer from 1 to 4.

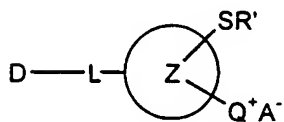
Especially preferred for use herein are thioglycolate ($\text{R}' = \text{CH}_2\text{COOH}$) thioethanol ($\text{R}' = (\text{CH}_2)_2\text{OH}$) and succinate ($\text{R}' = (\text{COOH})\text{CH}_2\text{CH}_2(\text{COOH})$), especially thioglycolate.

Thus preferred reactive dye compounds of the present invention comprise at least one chromophore moiety, at least one nitrogen-containing heterocycle and a linking group to link each chromophore moiety to each nitrogen-containing heterocycle characterised in

that the nitrogen-containing heterocycle is substituted with at least one thio-derivative and at least one quaternized nitrogen derivative. Suitable chromophore moieties, nitrogen-containing heterocycles, linking groups, thio-derivatives and quaternized nitrogen derivatives are as described above.

5

Especially preferred compounds having both a quaternized nitrogen derivative and a thio-derivative may be represented by the following formula (II):



10

wherein: D is a chromophore group as described hereinabove;

15

L is a linking moiety as defined herein, preferably selected from NR, NRC=O, NRSO₂, wherein R is as defined hereinabove;

Z is a nitrogen containing heterocycle as defined hereinabove;

20

SR' is a thio-derivative as described hereinabove,

Q⁺ is a quaternized nitrogen derivative as described hereinabove,

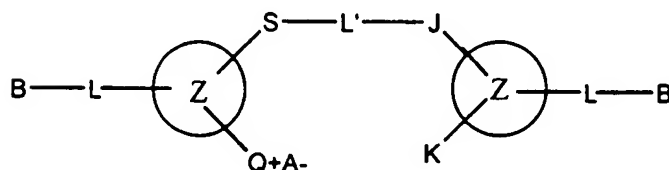
A is halogen, preferably chlorine or fluorine;

25

and salts and esters thereof.

Other preferred reactive dye compounds of the present invention can be represented by the formula (III):

30



wherein: B is a chromophore D as defined above, bifunctional chromophore, or other organic radical suitable for use in place of a chromophore such as those taught in the art (see for example EP-A-0,735,107), provided that the reactive dye compound contains at least one chromophore group.

35

Suitable B groups included β -sulphatoethylsulphonyl benzene, vinyl sulphonyl benzene, chloroethylsulphonyl benzene, β -s-thiosulphatoethyl sulphonyl benzene, di(ethylsulphonyl) chromophore

5 L, Z, Q, A are as defined hereinabove;

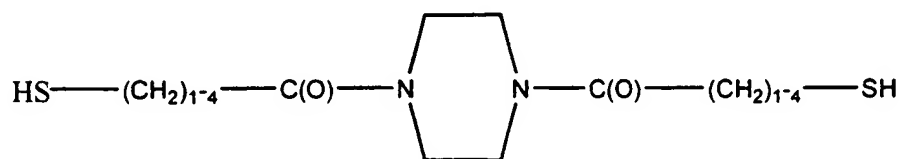
J is selected from S, O, NH

10 K is selected from Q^+ , halogen

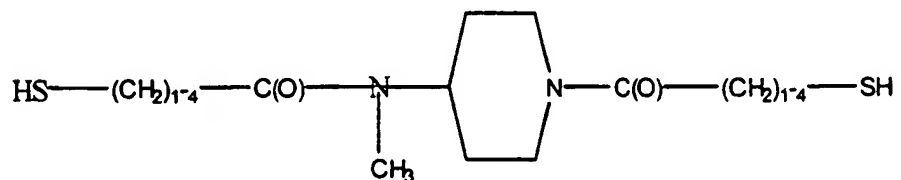
L' is a linking group which can be any suitable biradical linking group suitable for use in dye compounds and is preferably selected from B wherein B is as defined above, C1-C4 alkyl, esters having the formula (A1), diesters having the formula (A1), amides having the formula (A1),
15 diamides having the formula (A1) wherein A1 is $(CH_2)_{0-2}-(C(O)-J)_{0,1}-(CH_2)_{1-4}-(J-C(O))_{0,1}-(CH_2)_{0-2}-(J-C(O))-(C_1-C_4)-(C(O)-J)-$ where J is O, NH or S;

C1-C4 dialkyl sulphides, C1-C4 dialkylsulphoxides, C1-C4 dialkyl sulphones, C1-C4 dialkyl carboxylates, or groups having the formula:

20



or

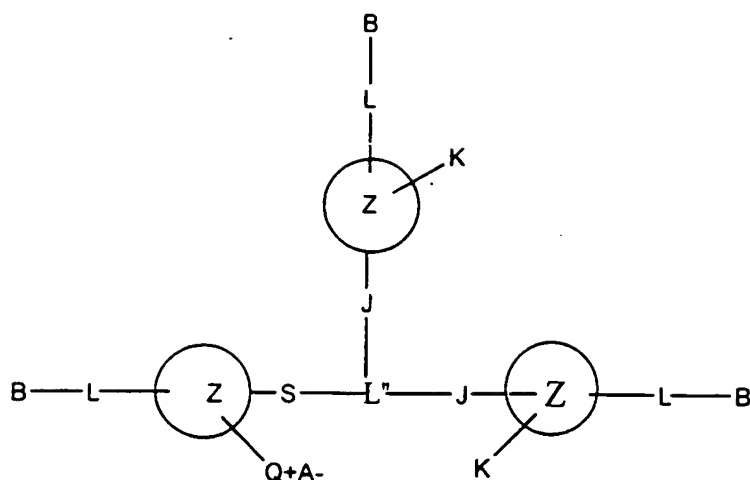


25

Suitable examples of L' include succinate, diethyl sulphide, β -sulphatoethylsulphonyl benzene, vinyl sulphonyl benzene, chloroethylsulphonyl benzene, β -s-thiosulphatoethyl sulphonyl benzene, di(ethylsulphonyl) chromophore, ethyl, diethylsulphone, isopropanol.

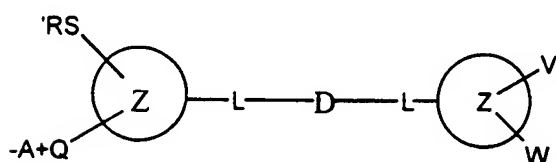
30

Another preferred reactive dye according to the present invention can be represented by compounds of the formula (IV):



wherein: B, L, Z, Q, K, J and A are as defined above and L'' is a linking group which can be any suitable triradical linking group suitable for use in dye compounds and is preferably selected from glycerol, diethylenetriamine and N,N',N'' tripropanoylamino-hexahydrotriazine provided that the reactive dye compound comprises at least one chromophore group.

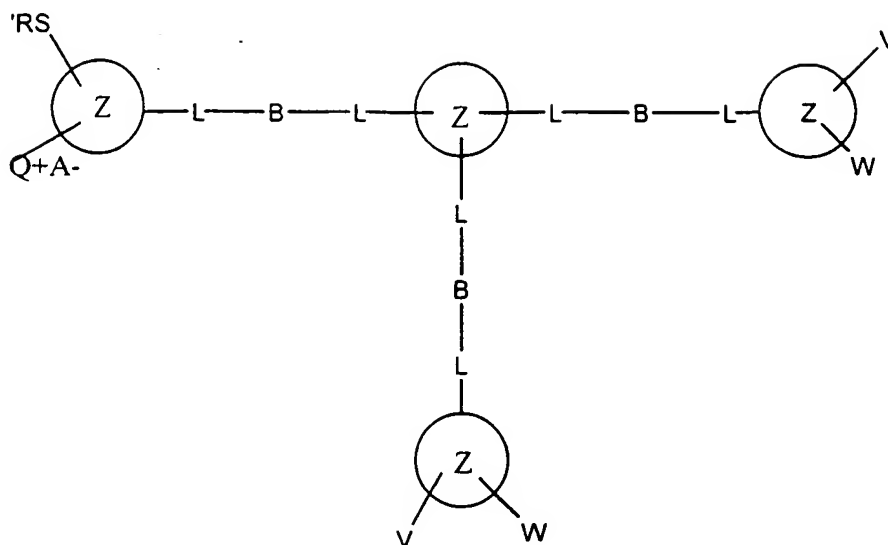
Another preferred reactive dye compound according to the present invention can be represented by compounds of the formula (V):



wherein: each of D, L, Z, R', Q are as defined above;

V and W are independently selected from NR, or SR' wherein R and R' are as defined hereinabove, Q⁺, halogen.

Another preferred reactive dye compound according to the present invention can be represented by compounds of the formula (VI):



wherein: each of B, Z, Q, A, R', L, V and W are as defined above, provided that
 5 the reactive dye compound contains at least one chromophore group.

In the above formulations it is to be noted that within each compound each of the defined groups may be the same or different. For example in formula V one of the Z groups may be pyrimidine and the other Z group may be triazine.

10 The dye compounds having the formula (I) can be prepared by reacting suitable precursors of the dye of formula (I) with one another, at least one of which contains a group D-L-pyrimidine, wherein D, and L are as defined above, and at least one of which contains a Q group (wherein Q is as defined above).

15 Dye compounds having the formula (I) wherein X is fluorine and Y is chlorine can be prepared by reacting a difluoromonochloro pyrimidine dye such as those commercially available from Clariant under the tradenames Drimalan (RTM) and Drimarene (RTM), with a suitable reactant containing a Q group.

20 In the preparation of dye compounds having the formula (I), the reactions of the starting dye compounds with the reactant containing a Q group are generally carried out at a pH of from about 5 to about 6, and at a temperature of about 40-45°C.

25 The reactive dyes having the formula (II) above can be prepared by reacting suitable precursors of the dye of formula (II) with one another, at least one of which contains a

group D-L-Z, wherein D, L and Z are as defined above, at least one of which contains an R' group (wherein R' is as defined above) and at least one of which contains a Q group (wherein Q is as defined above).

5 For example, dye compounds of the invention having a formula (II) wherein Z is a triazine heterocycle can be prepared by reacting a dichlorotriazine dye, such as those commercially available from BASF under the tradename Procion (RTM), with a suitable reactant containing an R' group and then reacting the intermediate dye compounds obtained with a suitable reactant containing a Q group.

10

Dye compounds of the invention having a formula (II) wherein Z is a pyrimidine heterocycle can be prepared by reacting a difluoromonochloro pyrimidine dye such as those commercially available from Clariant under the tradenames Drimalan (RTM) and Drimarene (RTM), with a suitable reactant containing an R' group and then reacting the intermediate dye obtained with a suitable reactant containing a Q group.

15

Dye compounds of the invention having a formula (II) wherein Z is a quinoxaline heterocycle can be prepared by reacting a dichloroquinolaxine dye such as those commercially available from Dystar under the tradename Levofix(RTM), with a suitable reactant containing an R' group and then reacting the intermediate dye obtained with a suitable reactant containing a Q group.

20

In the preparation of the dye compounds having the formula (II), the reactions of the starting dye compounds with the reactant containing an SR' group are generally carried out at a pH of from about 7 to about 10, and at a temperature of about 0-5 C. The reactions of the intermediate dye compounds with the reactant containing a Q group are generally carried out at a pH of from about 5 to about 6 and at a temperature of from about 50-85C. In particular, the reactions of the intermediate dye compounds with the reactant containing a Q group are generally carried out at temperature of from about 50-55C when Z is triazine and 75-85 C when Z is pyrimidine.

30

In general dyes having the formulae (II) - (V) can be prepared by using the same general chemistry as for dyes of formula (I) by reacting together suitable starting materials, and as exemplified below.

35

The dye compounds herein are suitable for dyeing and printing a wide variety of substrates, such as silk, leather, wool, polyesters, polyurethane, polyamide fibers and

polyurethanes, keratin fibres such as hair, and in particular cellulosic materials, such as the natural cellulose fibres, cotton, linen, hemp and the like, paper, and also cellulose itself and regenerated cellulose, and hydroxyl-containing fibres contained in blend fabrics, for example blends of cotton with polyester or polyamide fibres.

5

The dye compounds of the present invention can be applied and fixed to the substrate in various ways, in particular in the form of aqueous dye solutions and printing pastes. Thus according to the present invention there is provided a dye composition comprising one or more of the dye compounds described herein together with any carrier material

10

suitable for use in a dye composition.

Preferred dye compositions herein comprise an acidic buffer material. Any acidic buffer suitable for use in dye compositions can be used herein. An example of a suitable buffer is a mixed phosphate buffer.

15

When the dye composition herein is in the form of a paste a preferred ingredient is a thickening agent. Any suitable thickening agents suitable for use in dye compositions can be used herein.

20

When the dye composition is in the form of an aqueous solution or aqueous gel/paste, the dye composition preferably has a pH of about 5 or less, preferably from about 2 to about 3.

25

When the dye composition is being used for dyeing hair, the composition can comprise one or more of the compounds described herein either alone or in admixture with other well known hair dye compounds such as oxidative dyes, direct dyes, and the like.

30

The dyeing and printing processes which can be used with the dyes herein are conventional processes which are well known and which have been widely described in the technical and patent literature. The dye compounds herein are suitable for dyeing both by the exhaust method and also by the pad-dyeing method, whereby the goods are impregnated with aqueous, salt-containing or salt-free dye solutions and the dye is fixed after an alkali treatment or in the presence of alkali, if appropriate with the application of heat. The dye compounds herein are also suitable for the cold pad-batch method, after which the dye together with the alkali is applied to the pad-mangle and then fixed

35

by several hours of storage at room temperature. After fixing, the dyeings or prints are

thoroughly rinsed with cold and hot water, if appropriate with the addition of an agent acting as a dispersant and promoting the diffusion of the non-fixed portions.

Thus in accordance with another aspect of the present invention there is provided a use
5 of the reactive dyes of the present invention for dyeing and printing substrates such as cotton, wool, nylon, silk, keratin, leather, paper and the like. The compounds herein can be used in methods of dyeing all of the substrates listed above by applying an aqueous solution of one or more of the reactive dyes of the present invention to the substrate to be dyed under suitable conditions of pH and temperature.

10

The following examples serve to illustrate the compounds and compositions of the present invention.

The starting compounds and components given in the examples below can be used in
15 the form of the free acid or in the form of their salts.

Examples

Example 1

20

Synthesis of Monothioglycolatomonicotinyl triazine dye using Procion (RTM) dyes as starting materials

The monothioglycolatomonicotinyl triazine dye is prepared using the synthesis route
25 as illustrated in Diagram 1.

The synthesis consists of two parts, the first part for the preparation of monochloro-monothioglycolato triazine and the second part for the preparation of monothioglycolatomonicotinyl triazine as shown in the reaction mechanism below.

30

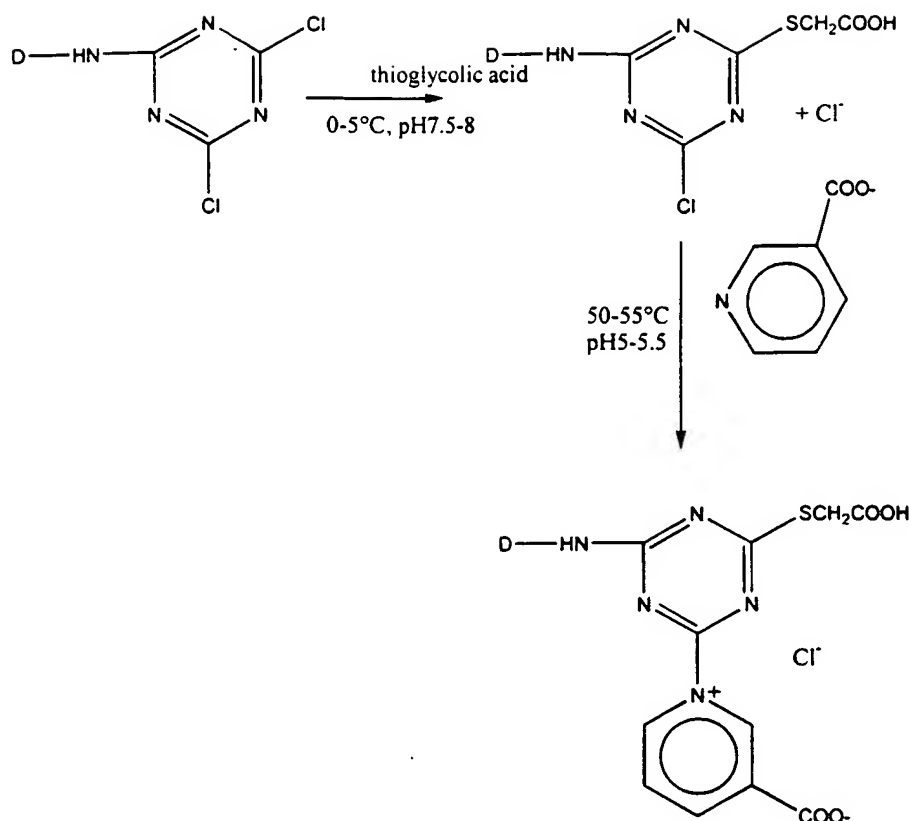


Diagram 1

5

In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example a variety of Procion (RTM) dyes commercially available from BASF are used as starting materials, in particular, Procion Red MX-8B, Procion Yellow MX-8G and Procion Blue MX-2G.

10

Synthesis of monochloromonothioglycolato triazine dye

The first part of the synthesis is to obtain monochloro-monothioglycolato triazine. An aqueous dye solution (0.1mol/100ml, pH 7.5) of a purified Procion (RTM) dichlorotriazine dye is prepared. To this solution, a 0.1mol solution of Mercaptoacetic acid is added by slow dripping at a temperature of between 0 and 5°C. After the addition of mercaptoacetic acid, the pH of the system is adjusted to 8 using sodium carbonate and HCl. The reaction is then allowed to proceed, at 0~5°C and pH8, for 5~8 hours. For each individual dye, the required reaction time is different (7~8 hours for Procion Red MX-8B, ~6 hours for Procion Yellow MX-8G and ~5 hours for Procion

20

Blue MX-2G). During the synthesis, a rapid pH drop is observed which is brought back up to pH 8 using the buffering agents. The end-of-reaction point, for this part of the synthesis, is indicated by the pH of the reaction system remaining constant for more than 5 minutes. At this point, the dye monochloro-monothioglycolato triazine is obtained. At the end of the synthesis, the pH of the system is reduced to below pH 2. The solid monochloromonothioglycolato triazine dye compounds is then obtained following precipitation and filtration.

Synthesis of Monothioglycolato mononicotinyl triazine dye

In the second part of the synthesis, the monochloro-monothioglycolato triazine obtained from the first part of the synthesis is reacted with nicotinic acid. An stoichiometric excess of an aqueous solution of nicotinic acid (pH 5~5.5) is added to an aqueous solution of monochloromonothioglycolato triazine dye solution. The temperature of the reaction system is then raised to 50~55°C and the pH adjusted to 5~5.5. The reaction is allowed to proceed, under these conditions, for a period of time. Again, a rapid drop in pH of the synthesis system is observed. The end-of-reaction point is, again, indicated by the stabilisation of the pH for more than 5 minutes. For each individual dye, the required reaction time is different (4~5 hours for Procion Red MX-8B, ~3 hours for Procion Yellow MX-8G and 2~2.5 hours for Procion Blue MX-2G). At this point, the monothioglycolato mononicotinyl triazine dye is obtained.

At the end of the synthesis, the reaction system is immediately cooled to below 5°C and its pH reduced below 2, in order to prevent the hydrolysis of monothioglycolato mononicotinyl triazine dye. The solid monothioglycolato mononicotinyl triazine dye is then obtained following precipitation and filtration.

The solid monothioglycolato mononicotinyl triazine dye obtained is rinsed with acetone 4~5 times to ensure they are free of water and then stored at 0~5°C.

Example 2

Synthesis of monothioglycolato monoisonicotinyl triazine dye

The monothioglycolato monoisonicotinyl triazine dye is prepared using the synthesis route illustrated in Diagram 2.

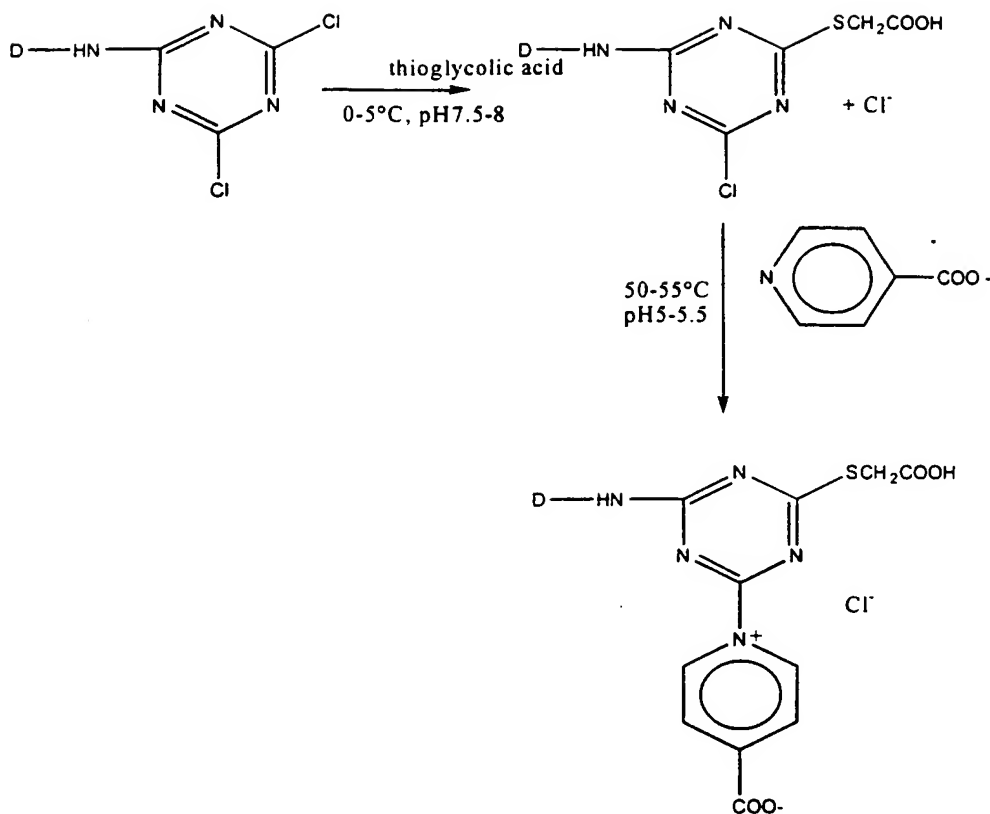


Diagram 2

In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example Procion (RTM) Red MX-8B is used as a starting material. The Procion Red MX-8B in this example can be substituted by other dichlorotriazine dyes such as Procion (RTM) Yellow MX-8G or Procion Blue MX-2G.

The synthesis consists of two parts, the first part for the preparation of monochloromonothioglycolato triazine dye and the second part for the preparation of monothioglycolatomonoisonicotinyl triazine dye.

Synthesis of monochloromonothioglycolato triazine dye

The preparation of monochloromonothioglycolato triazine dye is carried out in the same manner and using the same Procion starting dyes as described in Example 1 above.

Synthesis of monothioglycolatomonoisonicotinyl triazine dye

In the second part of the synthesis, the monochloromonothioglycolato triazine dye obtained from the first part of the synthesis is reacted with iso-nicotinic acid. 0.01 moles of the monochloromonothioglycolato triazine dye obtained from the first part of the synthesis is introduced to a flask together with 0.04 moles of isonicotinic acid in distilled water. The temperature of the reaction system is then raised to 55°C and the pH adjusted to 5.5. The reaction is allowed to proceed under these conditions for 30 minutes. Again, a rapid drop in pH of the synthesis system is observed which is raised again by the buffering agents. The endpoint of the reaction is indicated by the stabilisation of the pH for more than 5 minutes. The conditions of precipitation, filtration and acetone washing are the same as for the compound prepared in Example 1. The yield is over 85%.

15 Example 3Synthesis of Monothioglycolatomonodiazabicyclooctane triazine dye

The monothioglycolatomonodiazabicyclooctane triazine dye is prepared using the synthesis route as illustrated in Diagram 3.

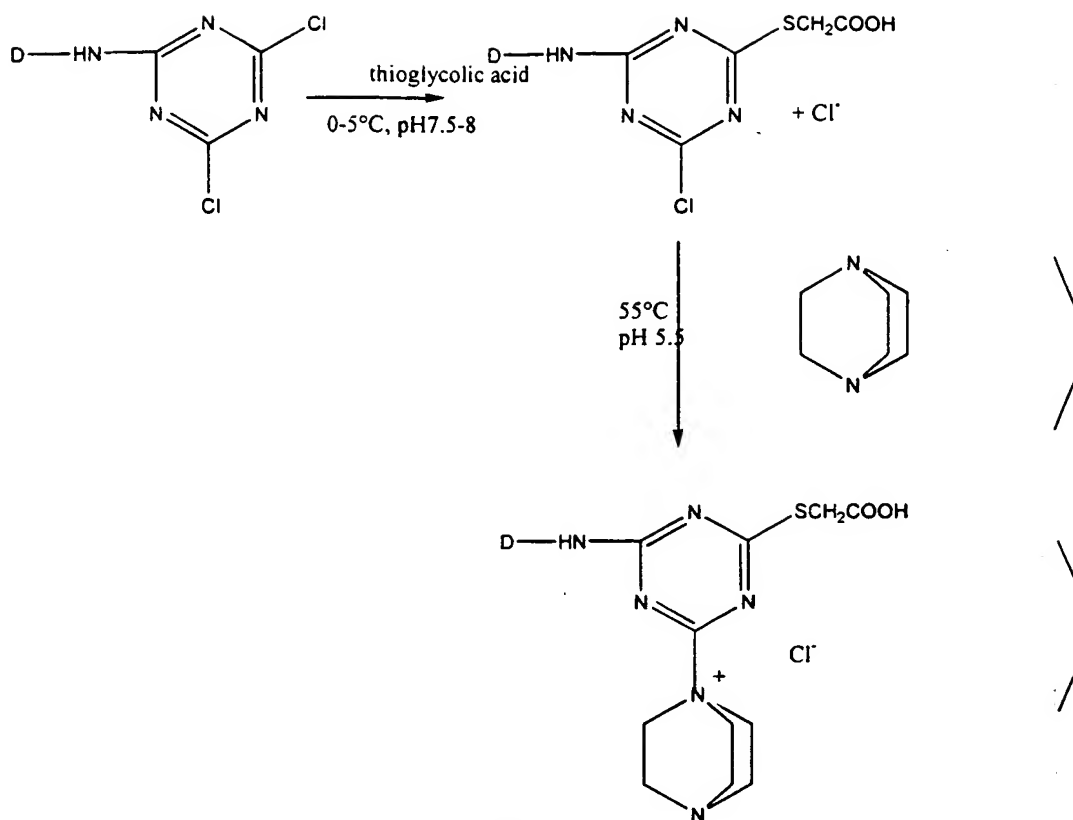


Diagram 3

In the reaction scheme D is a chromophore and varies depending on which starting dye
 5 is used. In the present example Procion (RTM) Red MX-8B is used as the starting material.

The synthesis consists of two parts, the first part for the preparation of
 monochloromonothioglycolatotriazine dye and the second part for the preparation of
 10 monothioglycolatomonoDABCO triazine dye. The preparation of
 monochlorothioglycolatotriazine is carried out in the same manner as described in
 Example 1 above.

In the second part of the synthesis, monochloromonothioglycolato triazine dye obtained
 15 from the first part of the synthesis is reacted with diazabicyclooctane (DABCO). 0.01
 moles of the monochloromonothioglycolato triazine dye is placed in a flask together
 with 0.03 moles of DABCO in distilled water. The temperature of the resulting solution
 is then raised to 55°C and the pH adjusted to 5.5. The reaction is allowed to proceed
 under these conditions for 15 minutes. Again, a rapid drop in pH of the synthesis
 20 system was observed which is brought back up to pH 5.5 by the buffering agents. The

end-point of the reaction is again indicated by the stabilisation of the pH for more than 5 minutes. The conditions of precipitation, filtration and acetone washing are the same as for Example 1 above. The yield is over 85%.

5 Example 4

Synthesis of monothioglycolatomonodimethylaminobetaine triazine dye

The monothioglycolatomonodimethylaminobetaine triazine dye is prepared using the
10 synthesis route as illustrated in Diagram 4.

15

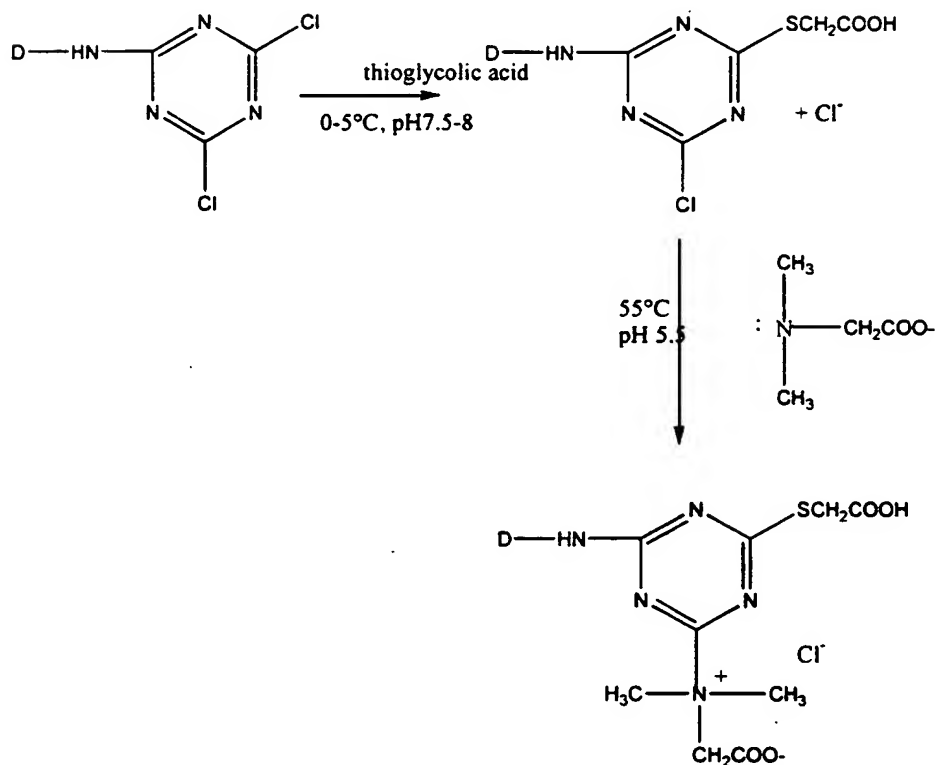


Diagram 4

20 In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example Procion (RTM) Red MX-8B is used as the starting material, but other suitable dichlorotriazine dye compounds can also be used as starting materials such as Procion (RTM) Yellow MX-8G and Procion (RTM) Blue MX-2G.

The synthesis consists of two parts, the first part for the preparation of monochloromonothioglycolatriazine dye and the second part for the preparation of monothioglycolatomonodimethylaminobetaine triazine dye. The preparation of monochlorothioglycolatriazine is carried out in the same manner as described in Example 1 above.

In the second part of the synthesis, monochloromonothioglycolato triazine dye obtained from the first part of the synthesis is reacted in aqueous solution with dimethylaminobetaine. 0.01 moles of monochloromonothioglycolato triazine dye is placed in a flask together with 0.01 moles of dimethylaminobetaine in distilled water. The temperature of the reaction system is then raised to 55°C and the pH adjusted to 5.5. The reaction was allowed to proceed under these conditions for 10 to 15 minutes. A rapid drop in the pH of the synthesis system was observed which is readjusted to pH 5.5 using the buffering agents. The endpoint of the reaction is indicated by the stabilisation of the pH for more than 5 minutes. The conditions of precipitation, filtration, and acetone washing are the same as for example 1 above. The yield is over 85%.

Example 5

Synthesis of monothioethanolmononicotinyl triazine dye

The monothioethanolmononicotinyl triazine dye is prepared using the synthesis route as illustrated in Diagram 5.

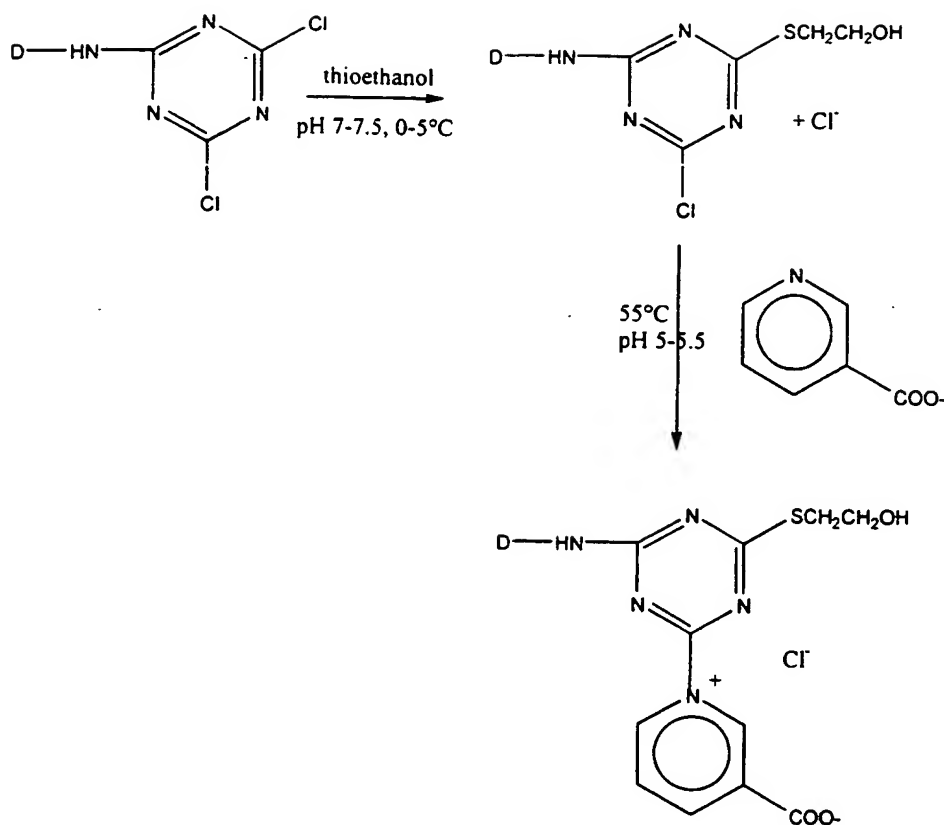


Diagram 5

In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example Procion (RTM) Red MX-8G was used as the starting material, but other suitable dichlorotriazine dye compounds can also be used as starting materials such as Procion Yellow MX-8G and Procion Blue MX-2G.

The synthesis consists of two parts, the first part for the preparation of monochloromonoethanol triazine dye and the second part for the preparation of monothioglycolatomonodimethylaminobetaine triazine dye.

Synthesis of Monochloromonoethanol triazine dye

0.1 mole of Procion Red MX-8G dye in distilled water is added to a flask. The flask is placed in an ice-water bath. 0.1 moles of thioethanol is then added drop-wise, to the reaction mixture under stirring. The total addition time is one hour. The pH of the reaction scheme is maintained at pH 7-7.5 and the temperature of the reaction system 0-5°C during addition of thioethanol. The reaction is then allowed to proceed at 0-5°C and pH 7.5-8 (which is corrected using sodium carbonate and HCl) for 5 hours. The

endpoint of the reaction is indicated by the pH remaining constant for more than 5 minutes. At this point, the monochloromonothioethanol triazine dye is obtained. Using 6N HCl, the pH of the system is then reduced to below pH2 to terminate the reaction. KCl (35% of the total solution) is then added to the reaction mixture in order to precipitate the dye. Filtration using Whatman filter paper followed. The precipitate is then washed with acetone for 4-5 times (50ml of acetone used each time) to obtain the final dye product.

Synthesis of monothioethanolmononicotinyl triazine dye

10

0.1 moles of monochloromonothioethanol triazine dye obtained from the above reaction is added to a flask together with 0.3 moles of nicotinic acid in distilled water. The temperature of the reaction system is then raised to 50-55°C and the pH adjusted to 5-5.5. The reaction is allowed to proceed under these conditions for 30 minutes. Again a rapid drop in pH is observed which is readjusted to pH 5-5.5 using buffering agents. The endpoint of the reaction is again indicated by the stabilisation of the pH for more than 5 minutes. The conditions of precipitation, filtration and acetone washing are the same as above in the first part of the synthesis. The yield is over 85%.

20 Example 6

Synthesis of monothiosuccinatemononicotinyl triazine dye

25 The monothiosuccinatemononicotinyl triazine dye is prepared using the synthesis route as illustrated in Diagram 6.

30

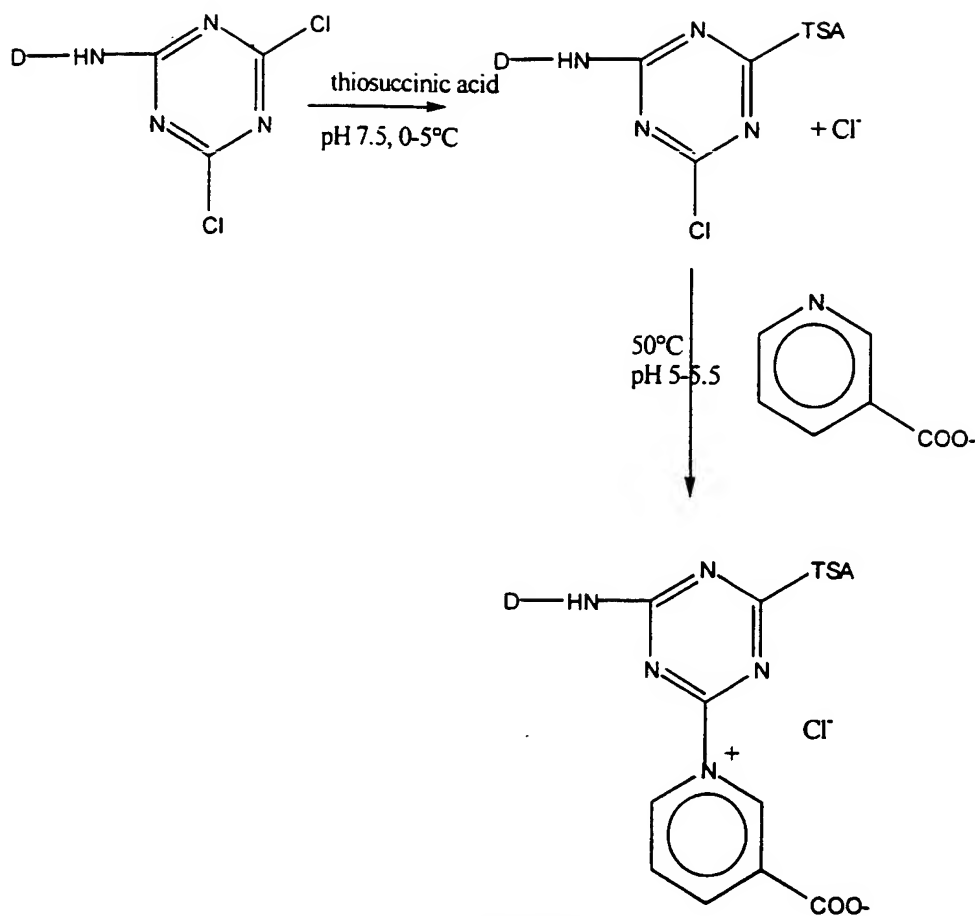


Diagram 4

In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example Procion (RTM) Red MX-8G is used as the starting material, but other suitable dichlorotriazine dye compounds can also be used as starting materials, such as Procion (RTM) Yellow MX-8G and Procion (RTM) Blue MX-2G. In the above reaction scheme TSA denotes thiosuccinate attached to the ring via its sulphur atom.

10

The synthesis consists of two parts, the first part for the preparation of monochloromonosuccinate triazine dye and the second part for the preparation of monosuccinatemononicotinyl triazine dye.

15

Synthesis of Monochloromonosuccinate triazine dye

0.1 moles of pure Procion Red MX-8G dye in distilled water are introduced into a flask. The flask was placed in an ice-water bath. 0.1 moles of thiosuccinic acid is then added

dropwise with stirring. The addition time is 1-1.5 hours. The pH of the reaction system is maintained at pH7.5 and the temperature of the reaction system is 0-5°C throughout the addition of thiosuccinic acid.

- 5 The reaction is then allowed to proceed, at 0-5°C and pH7.5-8 (which is corrected using sodium carbonate and HCl) for 6 hours. The endpoint of the reaction for this part of the synthesis is indicated by the pH of the reaction system remaining constant for more than 5 minutes. At this point, the dye monochloromonothiosuccinate triazine dye is obtained. Using 6N HCl, the pH of the system is then reduced to below pH 2 to
10 terminate the reaction. KCl (35% of the total solution) is then added to the reaction mixture in order to precipitate the dye. Filtration using Whatman paper followed. The precipitate is then washed with acetone for 4-5 times (50ml of acetone was used each time) to obtain the final dye product.

15 Synthesis of monothiosuccinatemononicotinyl triazine dye

- 0.01 moles of the monochloromonothiosuccinate triazine dye obtained from the first part of the synthesis is introduced to a flask together with 0.03 moles of nicotinic acid in distilled water. The temperature of the reaction system is then raised to 50°C and the
20 pH adjusted to 5-5.5. The reaction is allowed to proceed under these conditions for 15-20 minutes. Again a rapid change in the pH of the synthesis system is observed which is readjusted to pH 5-5.5 by addition of buffering agents. The endpoint of the reaction is indicated by the stabilisation of the pH for more than 5 minutes. The conditions of precipitation, filtration and acetone washing are the same as for Example 1. The yield is
25 over 85%.

Example 7

Synthesis of mono-5-chloro-2-nicotinyl-4-thioglycolato pyrimidine dye

- 30 The mono5-chloromono4-thioglycolato mono2-nicotinyl pyrimidine dye is prepared using the synthesis route as illustrated in Diagram 7.

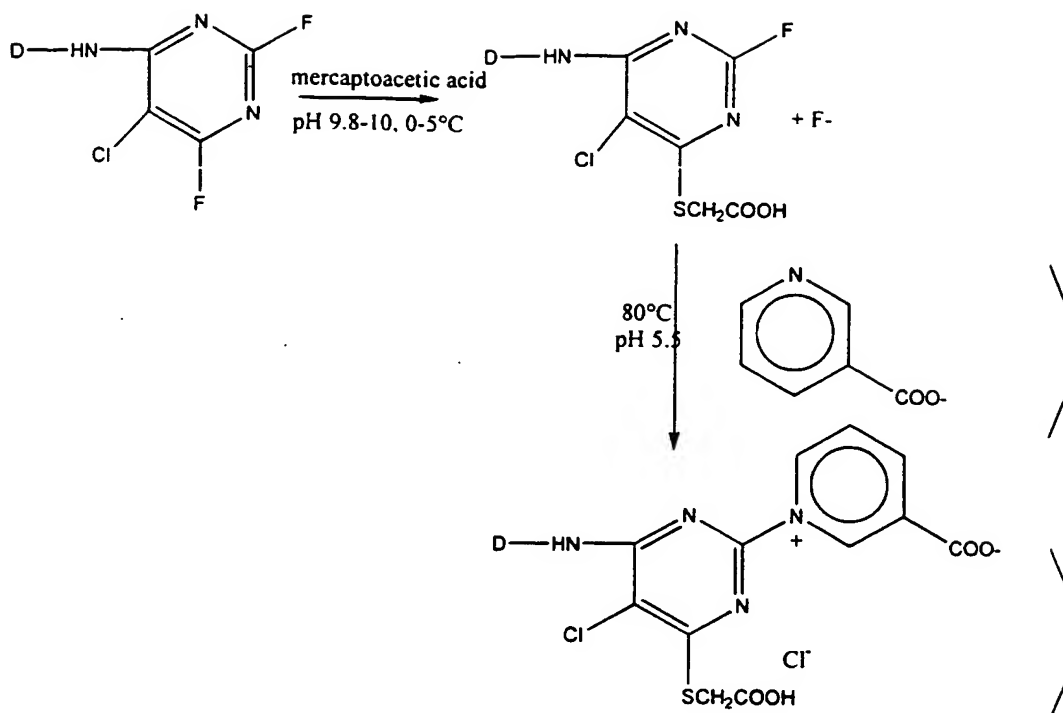


Diagram 7

In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example Drimalan (RTM) Red FB dye commercially available from Clariant is used as starting material. However, Drimalan Red FB can be substituted for any suitable difluoromonochloro pyrimidine dye such as those commercially available under the tradename Drimalan and Drimarene dyes, in particular, Drimalan Red FB, Drimalan Yellow F-R, Drimalan Blue F-G, Drimalan Blue F-B, Drimalan Yellow F-3GL, Drimalan Black F-B, Drimarene Golden Yellow R-G2R, Drimarene Blue R-GL, Drimarene Brill Red R-8B, and Drimarene Brill Red K-4BL. In the above reaction scheme TGA denotes a thioglycolato moiety.

The synthesis consists of two parts, the first part for the preparation of mono-5-chloromono-2-fluoromono-4-thioglycolato pyrimidine dye and the second part for the preparation of mono-5-chloro-2-nicotinyl-4-thioglycolato pyrimidine dye.

Synthesis of mono-5-chloromono-2-fluoromono-4-thioglycolato pyrimidine dye

0.1 moles of Drimalan Red F-B dye in distilled water are introduced into a flask. The flask is then placed in an ice-water bath. 0.1 moles of mercaptoacetic acid is then added dropwise to the reaction mixture with stirring. The total addition time is 1-1.5 hours.

The pH of the reaction mixture is maintained at pH 9.8-10 and at a temperature of 0-5°C throughout the addition of mercaptoacetic acid.

5 The reaction is then allowed to proceed at 5°C and pH 9.8-10 (which is corrected using sodium carbonate and HCl) for 15 hours. The end-of-reaction point for this part of the synthesis is indicated by the pH of the reaction system remaining constant for more than 5 minutes. At this point, the mono-5-chloro-2-fluoro-mono-4-thioglycolato pyrimidine dye is obtained. Using 6N HCl the pH of the system is then reduced to below pH2 to terminate the reaction. KCl (\cong 35% of the total solution) is then added to the reaction
10 mixture in order to precipitate the dye. Filtration using Whatman filter paper followed. The precipitate is then washed with acetone for 4-5 times (\cong 50ml of acetone used each time) to obtain the mono-5-chloro-2-fluoro-mono-4-thioglycolato pyrimidine dye.

Synthesis of mono-5-chloro-2-nicotinyl-4-thioglycolato pyrimidine dye

15 0.1 moles of the mono-5-chloro-mono-2-fluoro-4-thioglycolato pyrimidine dye in distilled water prepared in the first part of the synthesis is reacted with 0.3 moles of nicotinic acid. The temperatures of the reaction system is then raised to $80 \pm 1^\circ\text{C}$ and the pH adjusted to 5.5. The reaction is allowed to proceed under these conditions for 3-
20 4 hours. Again a rapid change of the pH of the synthesis system is observed. The end point of the reaction is indicated by the stabilisation of the pH for more than 5 minutes. The conditions of precipitation, filtration and acetone washing are the same as in the first part of the synthesis. The yield is over 85%.

25 Example 8

Synthesis of 5-chloro-4-nicotinyl-2-thioglycolato pyrimidine dye

30 The 5-chloro-4-nicotinyl-2-thioglycolato pyrimidine dye is prepared using the synthesis route as illustrated in Diagram 8.

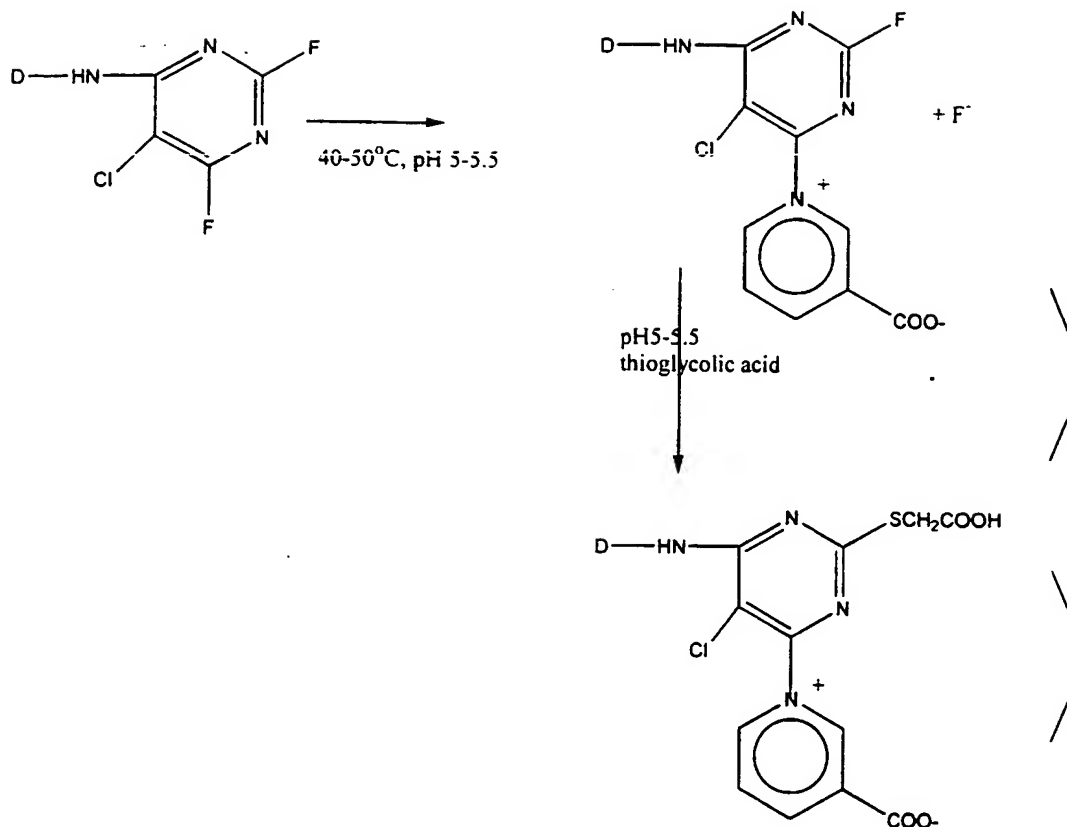


Diagram 8

- 5 In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example Drimarene Brill Red 4-KBL is used as the starting material. Drimalan Red FB can be substituted for a variety of other suitable difluoromonochloro pyrimidine dyes or trichloro pyrimidine dyes such as those commercially available from Clariant under the tradenames Drimalan and Drimarene, including Drimalan Red F-B, Drimalan Yellow F-R, Drimalan Blue F-G, Drimalan Blue F-B, Drimalan Yellow F-3GL, Drimalan Black F-B, Drimarene Golden Yellow R-G2R, Drimarene Blue R-GL, and Drimarene Brill Red R-8B. In the above reaction scheme TGA denotes a thiolglycolato moiety.
- 10
- 15 The synthesis consists of two parts, the first part for the preparation of 5-chloro-4-nicotinyl-2-fluoro pyrimidine dye and the second part for the preparation of 5-chloro-4-nicotinyl-2-thioglycolato pyrimidine dye.

Synthesis of 5-chloro-4-nicotinyl-2-fluoro pyrimidine dye

0.1 moles of pure Drimarene Brill Red K-4BL dye and 150ml of distilled water are introduced into a flask. 0.1 mole of nicotinic acid is then added dropwise to the reaction mixture under stirring, from a dripping funnel. The total addition time is 1-1.5 hours. The pH of the reaction system is maintained at pH 5-5.5 and the temperature of the reaction system 40-45°C, throughout the addition of nicotinic acid.

The reaction is then allowed to proceed at 40-45°C and pH 5-5.5 (which was corrected using sodium carbonate and HCl) for 3-4 hours. The end-of-reaction point for this part of the synthesis is indicated by the pH of the reaction system remaining constant for more than 5 minutes. At this point, the 5-chloro-4-nicotinyl-2-fluoro pyrimidine dye is obtained. Using 6N HCl, the pH of the system is then reduced to below pH 2 to terminate the reaction. KCl (\cong 35% of the total solution) is then added to the reaction mixture in order to precipitate the dye. Filtration using Whatman filter paper follows. The precipitate is then washed with acetone 4-5 time (\cong 50ml of acetone is used each time) to obtain the 5-chloro-4-nicotinyl-2-fluoro pyrimidine dye.

Synthesis of 5-chloro-4-nicotinyl-2-thioglycolato pyrimidine dye

0.1 moles of the 5-chloro-4-nicotinyl-2-fluoro pyrimidine dye obtained from the first part of the synthesis is dissolved in water and introduced into a 400ml flask. 0.1 moles of mercaptoacetic acid is then added dropwise to the reaction mixture with stirring. The total addition time is 1-1.5 hours. The pH of the reaction scheme is maintained at pH 5-5.5 and the temperature of the reaction system 50-55°C throughout the addition of mercaptoacetic acid.

The reaction is then allowed to proceed at 50-55°C and pH 5-5.5 (which is corrected using sodium carbonate and HCl) for 32-35 hours. The end-of-reaction point for this part of the synthesis is indicated by the pH of the reaction system remaining constant for more than 5 minutes. At this point, 5-chloro-4-nicotinyl-2-thioglycolato pyrimidine dye is obtained. Using 6N HCl, the pH of the system is then reduced to below pH 2 to terminate the reaction. KCl (\cong 35% of the total solution) is then added to the reaction mixture in order to precipitate the dye. Filtration using Whatman filter paper follows. The precipitate is then washed with acetone for 4-5 times (\cong 50ml of acetone used each time) to obtain the final dye product.

Example 9

Synthesis of nicotinylthioglycolato quinoxaline dye

The nicotinylthioglycolato quinoxaline dye is prepared using the synthesis route as illustrated in Diagram 9.

- 5 The synthesis consists of two parts, the first part for the preparation of monothioglycolato quinoxaline dye and the second part for the preparation of monothioglycolato mononicotinyl quinoxaline dye as shown in the reaction mechanism below.

10

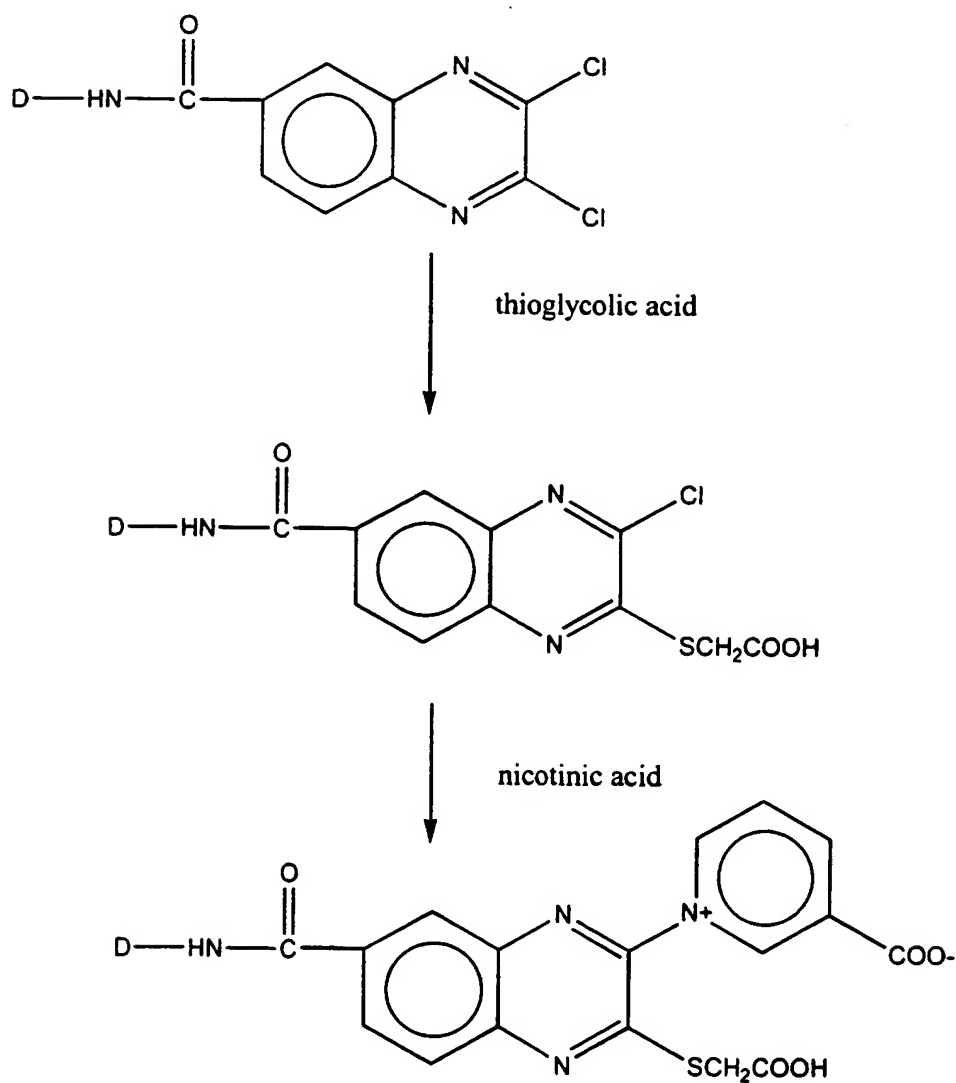


Diagram 9

In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example, Levafix Goldgelb E-G commercially available from DyStar is used a starting material but this can be replaced by any suitable quinoxaline dye such as Levafix Brilliant Blue E-B, Levafix Brilliant Red E-RN and Levafix Brown E-2R.

Synthesis of monothioglycolatoquinoxaline dye

0.1 moles of pure Levafix Goldgelb E-G dye in distilled water is introduced into a flask. 0.1 moles of mercaptoacetic acid is then added dropwise to the reaction mixture with stirring. The total addition time is 1 hour. The pH of the reaction system is maintained at pH 9 and the temperature of the reaction system 30-35°C throughout the addition of mercaptoacetic acid.

The reaction is then allowed to proceed at 30-35°C and pH 9 (which was corrected using sodium carbonate and HCl) for 4-5 hours. The end-of-reaction point for this part of the synthesis is indicated by the pH of the reaction system remaining constant for more than 5 minutes. At this point, thioglycolato quinoxaline dye is obtained. Using 6N HCl, the pH of the system is then reduced to below pH2 to terminate the reaction.

KCl ($\approx 35\%$ of the total solution) is then added to the reaction mixture in order to precipitate the dye. Filtration using Whatman filter paper follows. The precipitate is then washed with acetone for 4-5 times ($\approx 50\text{ml}$ of acetone used each time to obtain the dye product).

Synthesis of nicotinylthioglycolato quinoxaline dye

0.1 moles of the dye obtained from the first part of the synthesis and 0.3 moles of nicotinic acid are dissolved in distilled water in a flask. The temperature of the reaction system is then raised to 50-65°C and the pH adjusted to 4-4.5. The reaction is allowed to proceed under these conditions for 5-6 hours. Again a rapid change of the pH of the synthesis system is observed. The end-of-reaction point is again indicated by the stabilisation of the pH for more than 5 minutes. The conditions of precipitation, filtration and acetone washing are the same as above. The yield is over 85%.

Example 10

Synthesis of Compound 10C

The dye denoted by 10C is prepared using the synthesis route as illustrated in Diagram 10.

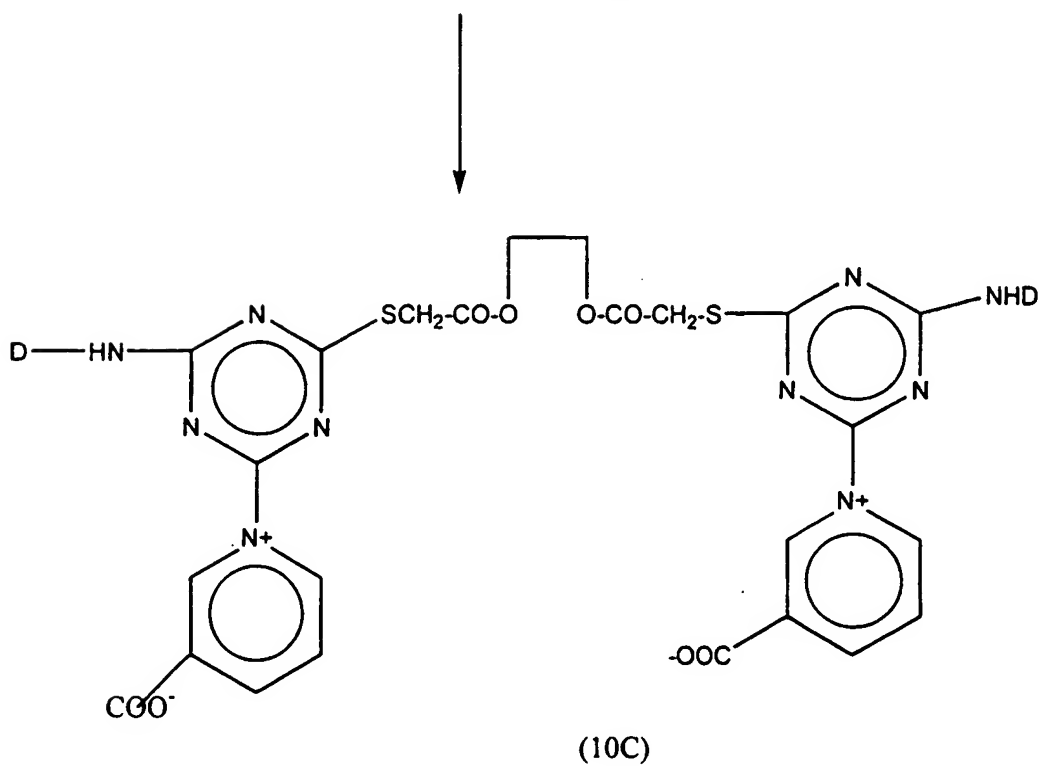
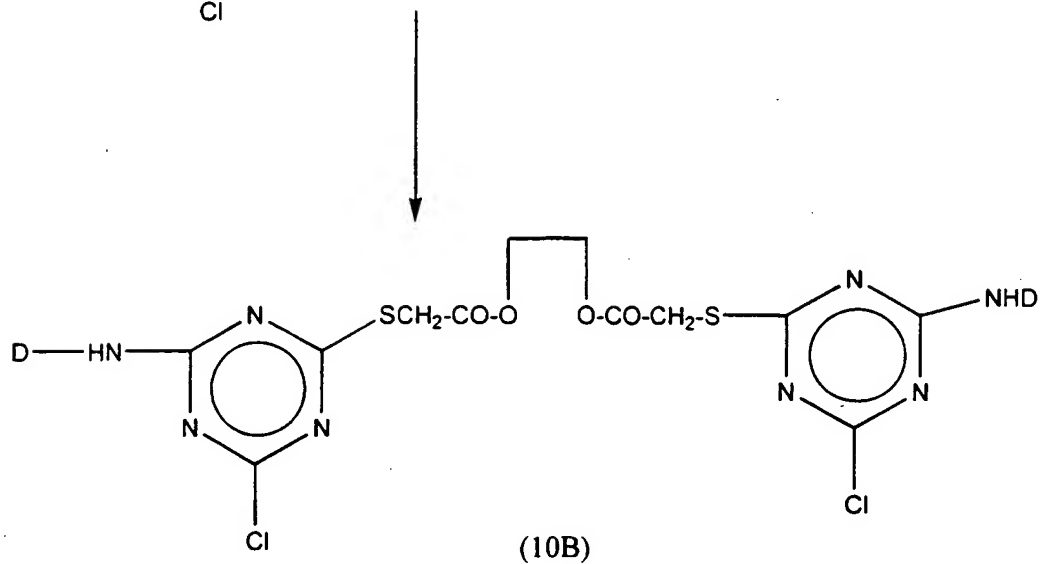
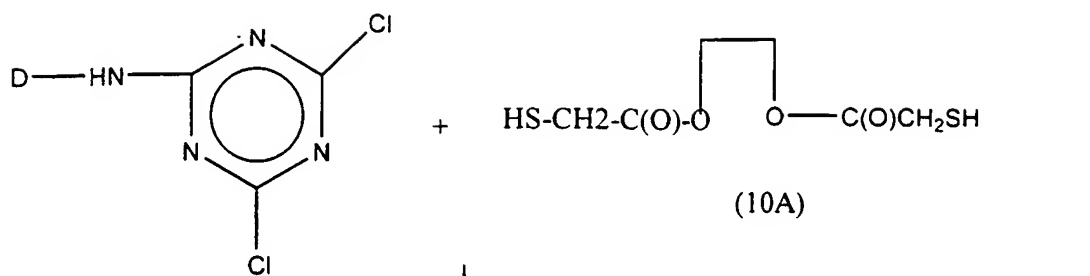


Diagram 10

- In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example, Procion Red MX-8B commercially available from BASF is used a starting material but this can be replaced by any suitable triazine dye such as Procion Yellow MX-8G and Procion Blue MX-2G.

Synthesis of 10B

- 0.2 moles of Procion Red MX-8B dye is dissolved in water and reacted with 0.1 moles of ethylene glycol-bis-thioglycolate by stirring at 0-5°C and maintaining the pH at 7.0 (additions of NaHCO₃ as required) for 6 hours (or until the pH remains constant). The product of this reaction is compound 10B.

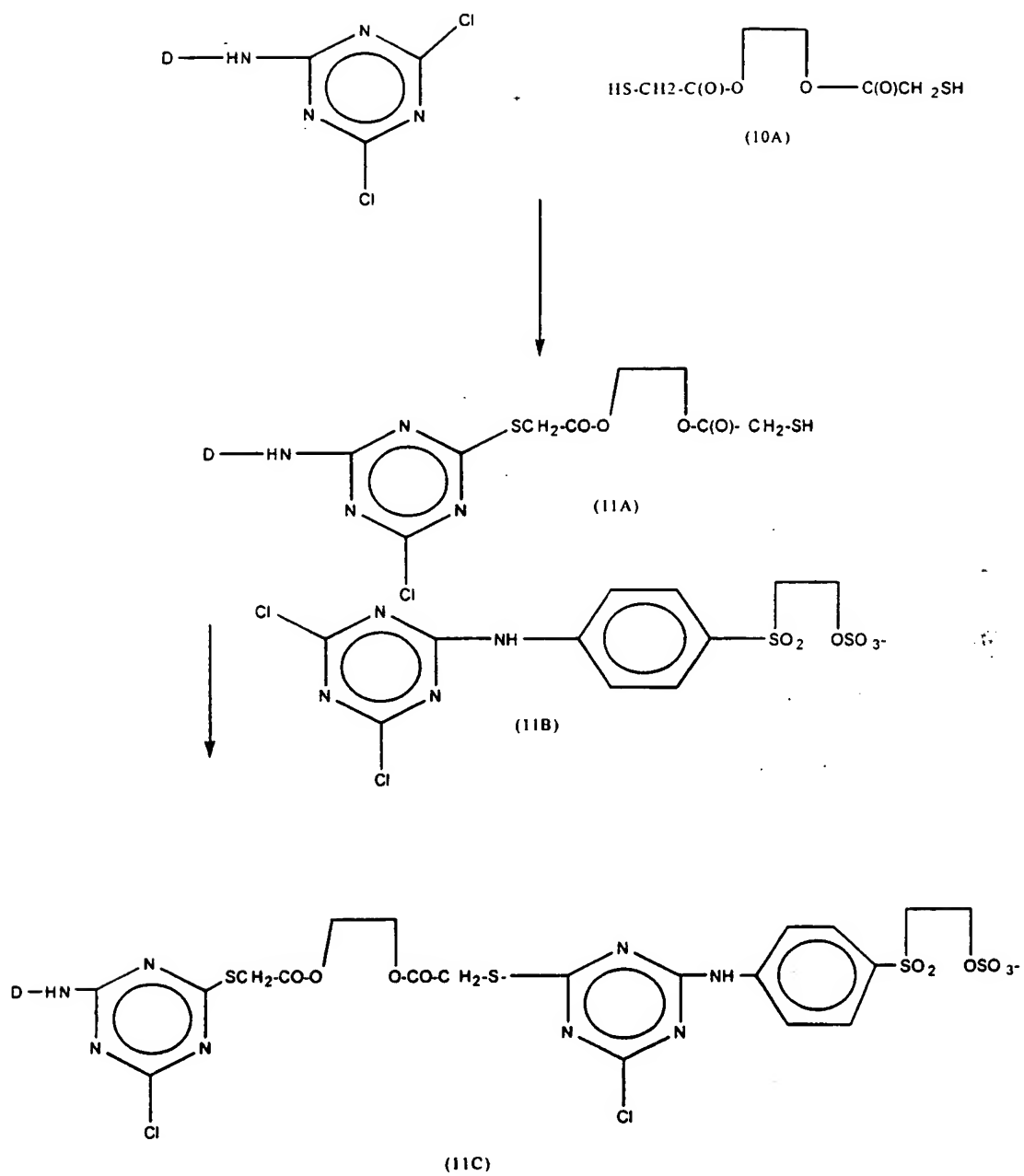
Synthesis of 10C

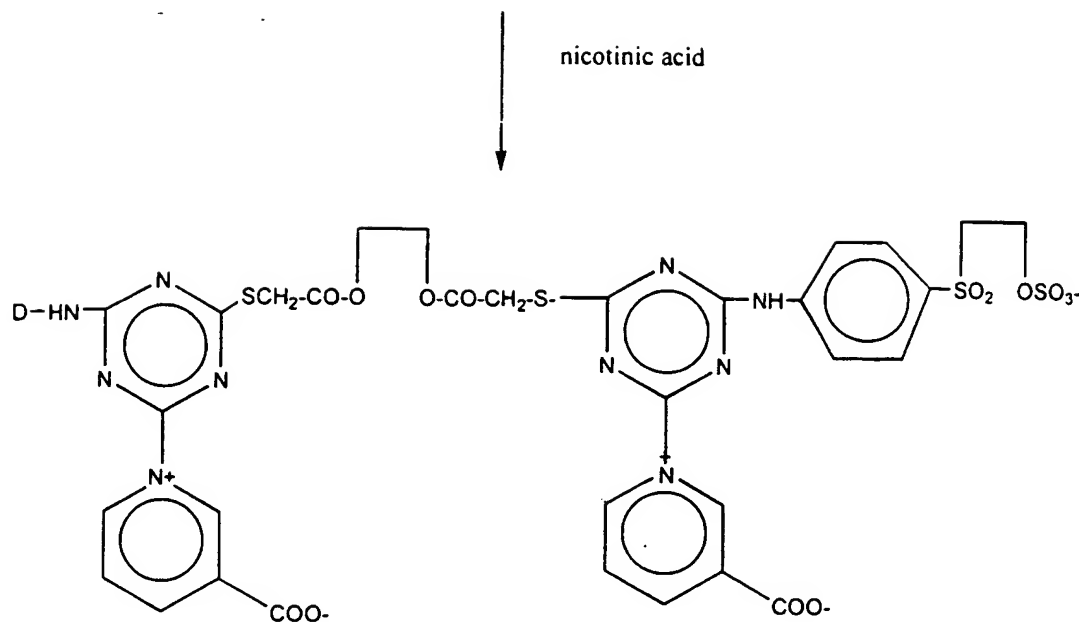
- Compound 10B is then reacted with 0.3 moles of nicotinic acid at pH 5-5.5 at 50-55°C for 4 hours (or until the pH remains constant).
- At this point the pH of the aqueous dye solution is reduced to 2.0 and the solution cooled to below 5°C. The required dye 10C is filtered off and dried.

Example 11

- Synthesis of dye compound 11D

45





(11D)

In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example, Procion Red MX-8B commercially available from BASF is used a starting material but this can be replaced by any suitable triazine dye
 5 such as Procion Yellow MX-8G and Procion Blue MX-2G.

0.1 mole of Procion Red MX-5B is dissolved in water and slowly added to a chilled stirred aqueous solution of 0.1 moles of ethylene glycol-bis-thioglycolate. The solution
 10 temperature is 0-5°C and is maintained at this temperature. The solution is maintained at pH 7 throughout the reaction by the addition of sodium bicarbonate. The intermediate dye 11A is formed when the pH stabilizes.

An aqueous solution of p-aminobenzenesulphatoethylsulphone is prepared and
 15 maintained at pH 6-7 and 0-5°C. Cyanuric chloride is then added to this solution to give a compound having the formula (11B):

0.1 moles of compound 11B is then slowly added to an aqueous solution of the
 20 intermediate dye 11A, maintaining the pH at 7 and the temperature at 0-5°C. When the pH is stabilized (5-6 hours), the reaction is complete. The product from this reaction

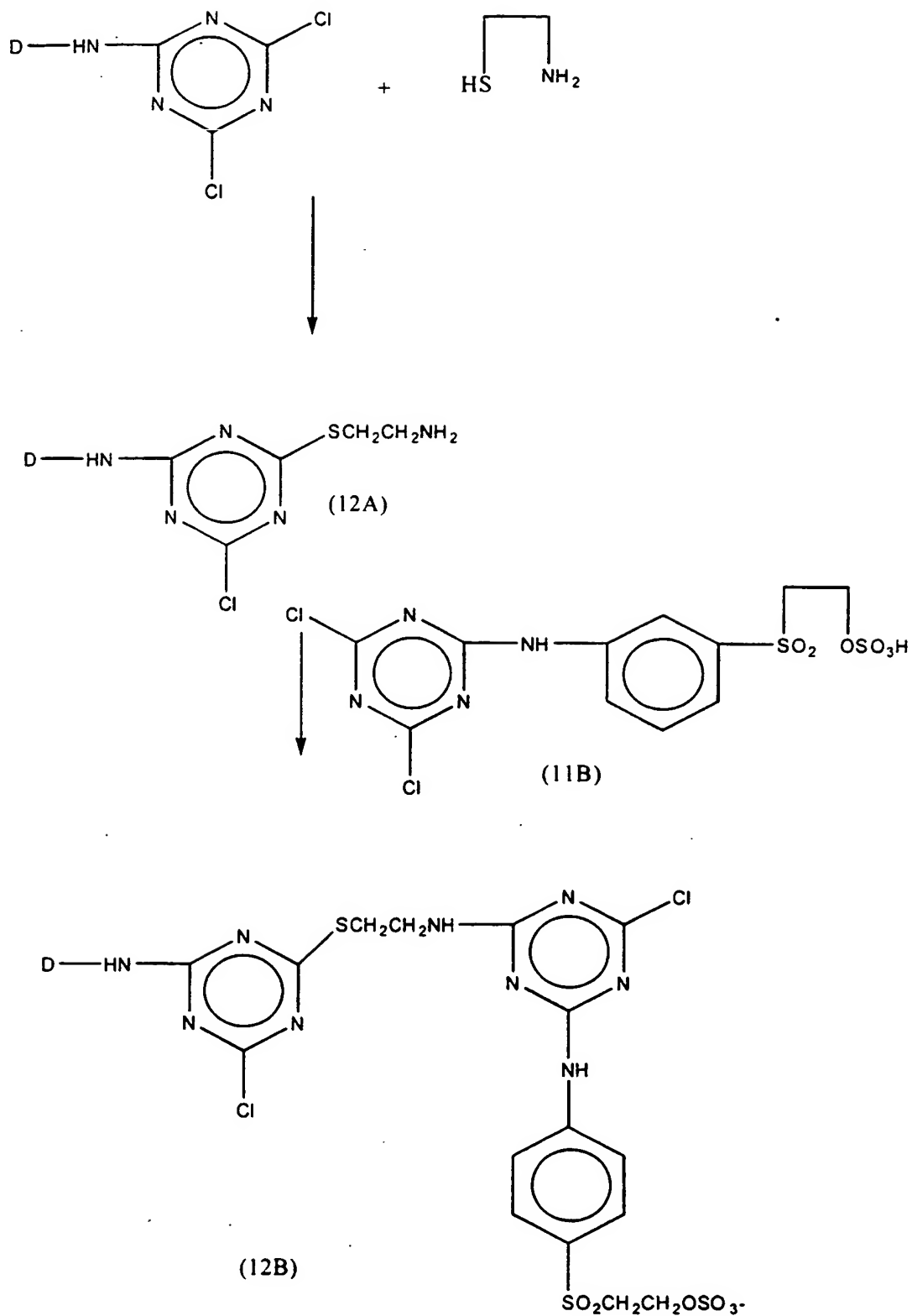
(11C) is then reacted with 0.3 moles of nicotinic acid at pH 5-5.5 at 50-55°C for 5 hours or until the pH remains constant to produce the final dye compound 11D.

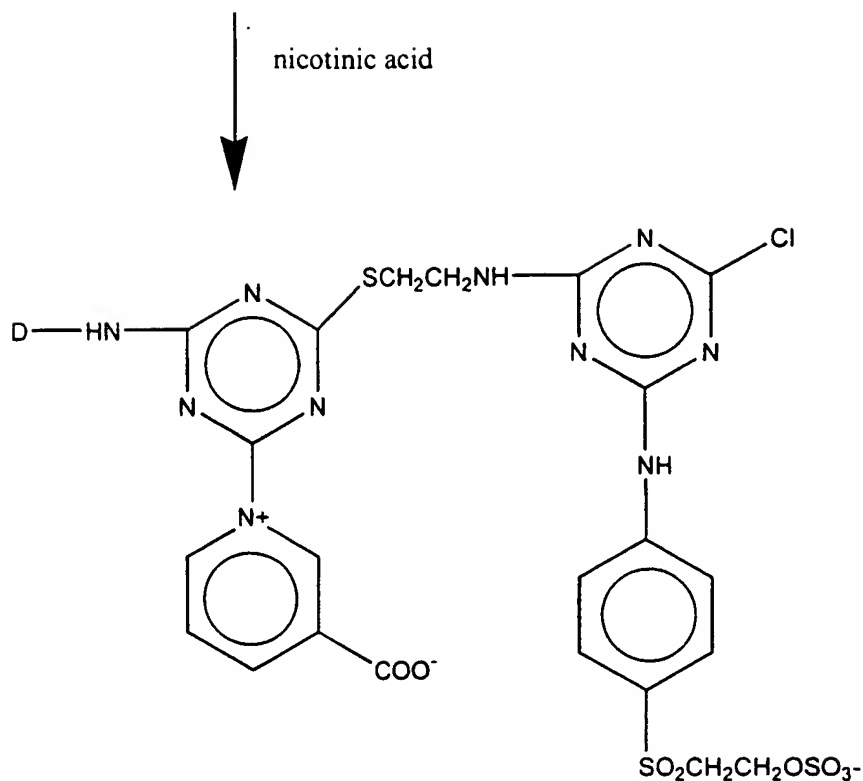
5 Example 12

Synthesis of 12C

The synthesis takes place according to the following reaction mechanism:

48





In the reaction scheme D is a chromophore and varies depending on which starting dye
 5 is used. In the present example, Procion Yellow MX-8G commercially available from
 BASF is used a starting material but this can be replaced by any suitable triazine dye
 such as Procion Red MX-8B and Procion Blue MX-2G.

An aqueous solution of Procion Yellow MX-8G (0.1 mole) is slowly added to an
 10 aqueous solution of 0.1 cystamine at pH6 and 0-5°C. The pH is maintained at pH 6 by
 the addition of NaHCO₃. After 4 hours the pH stabilizes and the reaction is complete.
 Dye intermediate 12A is obtained.

0.1 moles of compound 11B prepared in example 11 is then slowly added to 0.1 moles
 15 of aqueous solution of dye 12A at 30°C and pH7. After 2 hours the pH stabilizes.
 Quaternization of the resulting product 12B is then carried out by reaction at 50°C and

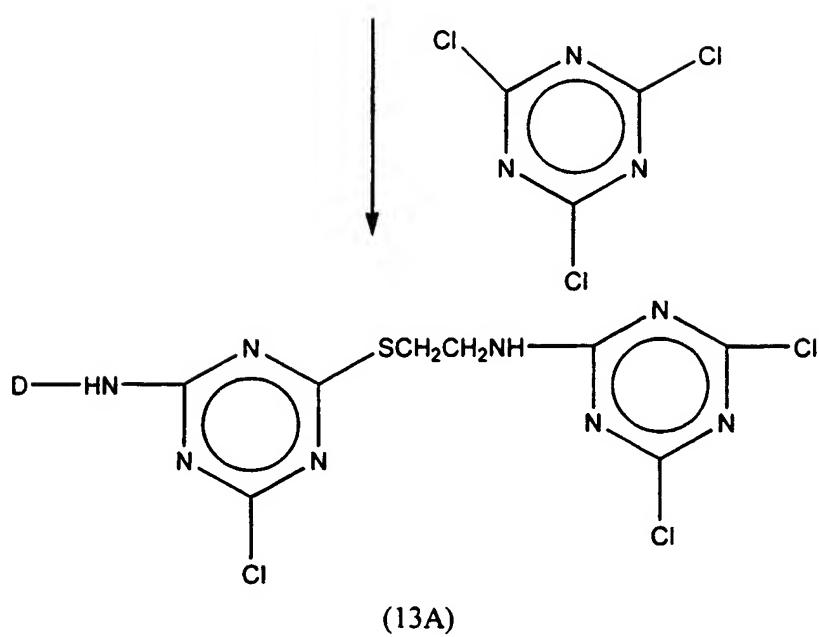
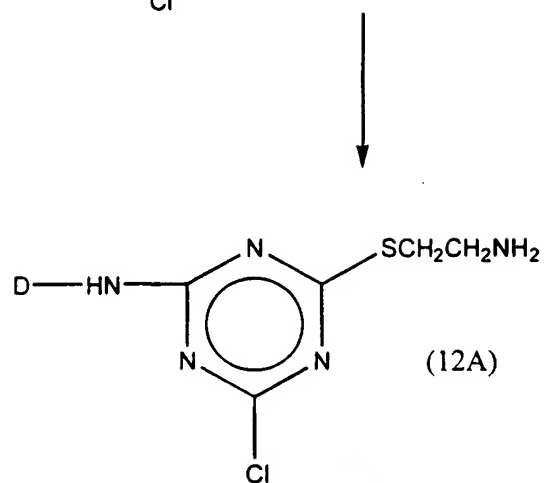
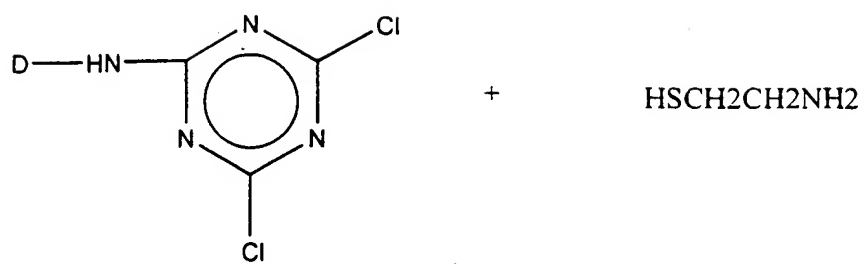
pH 5 with 0.3 moles of nicotinic acid. The reaction is complete when the pH has stabilized. The final dye 12C is isolated by cooling to 5°C and filtered off.

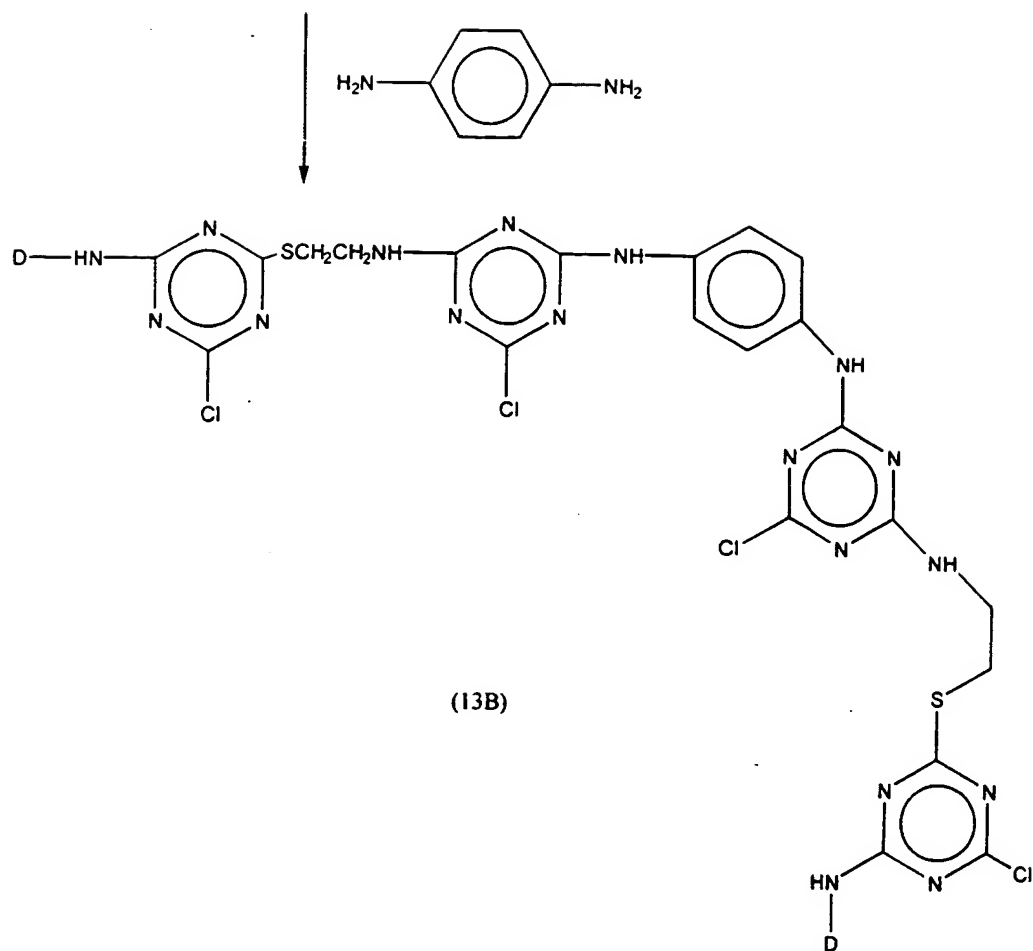
Example 13

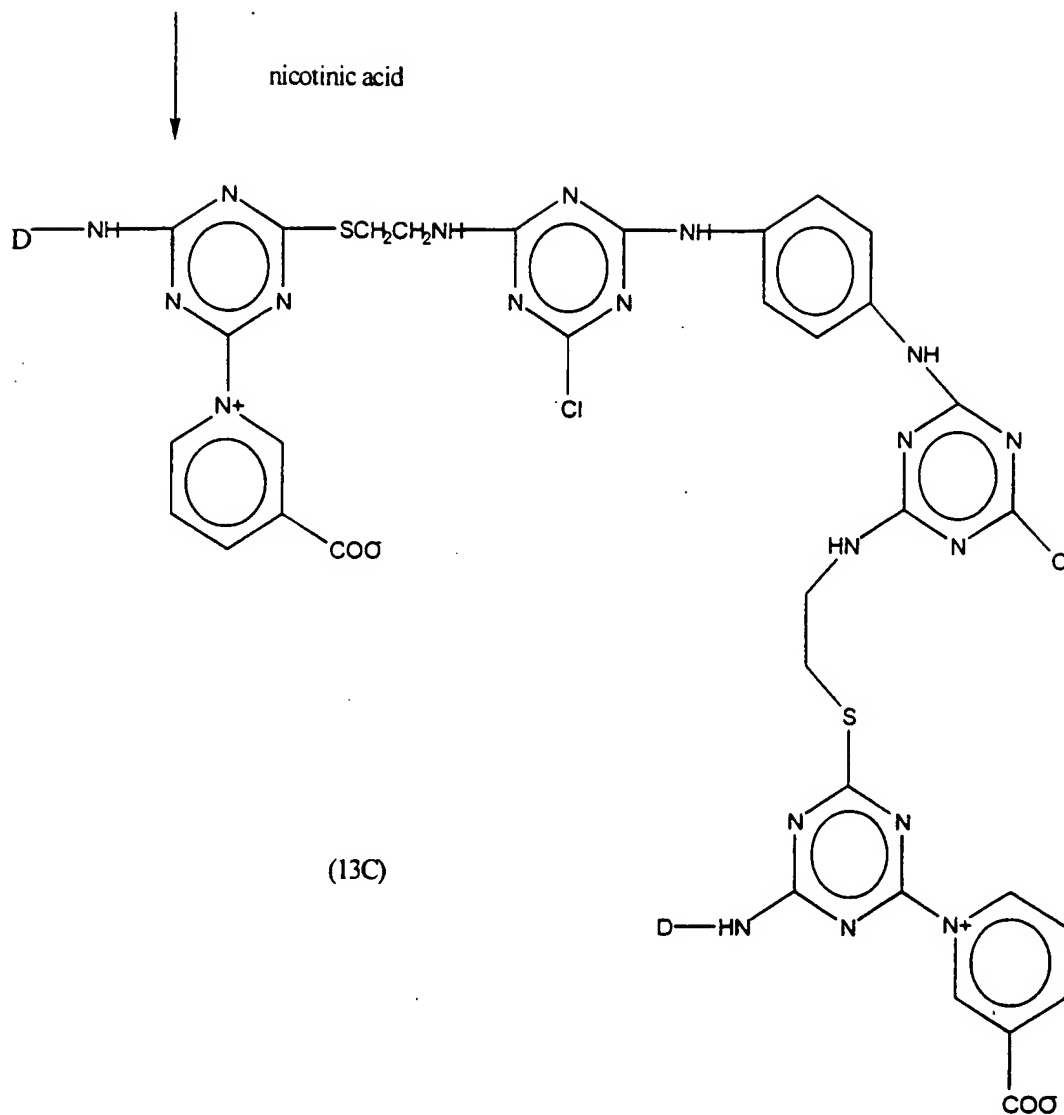
5

Synthesis of Compound 13B

The dye compound 13B is synthesised according to the reaction mechanism below.







In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example, Procion Yellow MX-8G commercially available from BASF is used a starting material but this can be replaced by any suitable triazine dye such as Procion Red MX-8B and Procion Blue MX-2G.

0.1 moles of cyanuric chloride in acetone was slowly added over 30 minutes to 0.1 moles of compound 12A in aqueous solution at 0-5°C at pH7. When the pH stabilised the reaction was complete and compound 13A was obtained.

0.1 moles of compound 13A was dissolved in water and added to aqueous solution of p-phenylene diamine (0.05 moles) while maintaining the pH and 6 and temperature at 30°C. After 30 minutes the pH stabilizes and compound 13B is obtained.

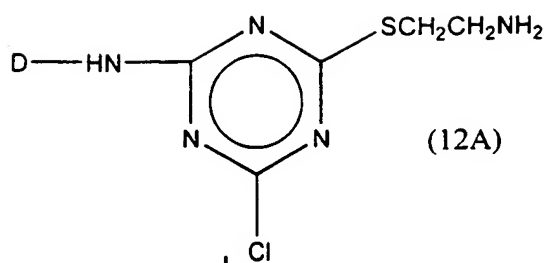
- 5 0.5 moles of nicotinic acid is then added to an aqueous solution of compound 13B. The pH was maintained at 5 and the temperature at 50°C. After 4 hours the pH was judged to be stabilized and compound 13C was obtained.

Example 14

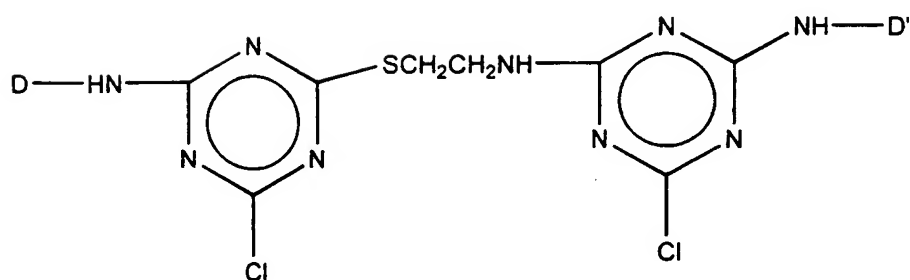
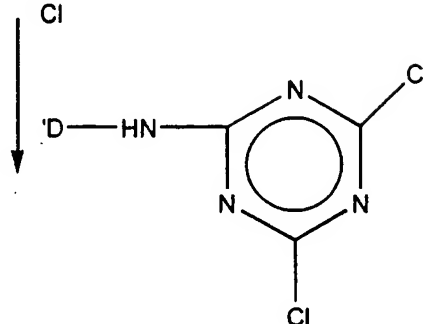
10

Compound 14B is prepared by the reaction mechanism below.

55

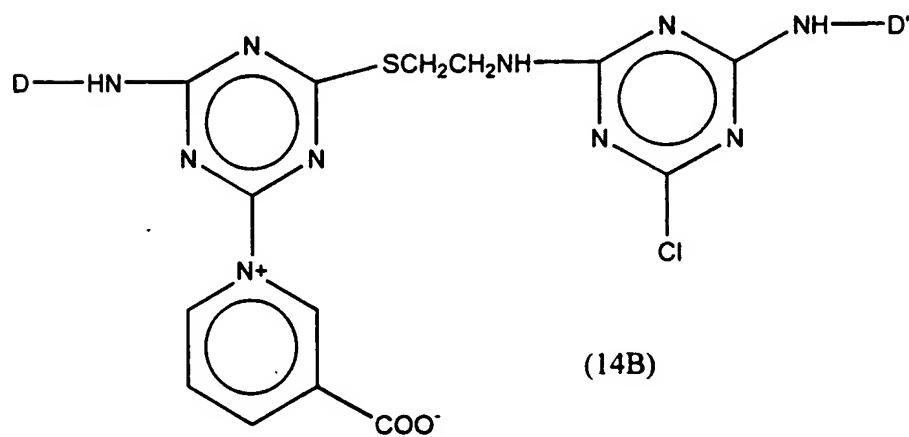


(12A)



(14A)

nicotinic acid



(14B)

In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example, Procion Yellow MX-8G commercially available from BASF is used a starting material but this can be replaced by any suitable triazine dye such as Procion Red MX-8B and Procion Blue MX-2G. In the reaction scheme D' is a chromophore and varies depending on which starting dye is used. In the present example, Procion Red MX-8B was used but this can be replaced by any suitable triazine dye.

0.1 moles of compound 12A is reacted with 0.1 moles of Procion Red MX-8B at pH 7 and 30°C for 2 hours. The pH is maintained at 7 by the addition of NaHCO₃. Compound 14A was obtained.

0.1 moles of Compound 14A is then reacted with 0.2 moles of nicotinic acid at 50°C and pH 5 for 2 hours. When the pH stabilizes compound 14B is produced.

Example 15

The 5-chloro-4-nicotinyl-2-fluoro pyrimidine dye is prepared using the synthesis route as illustrated in Diagram 15.

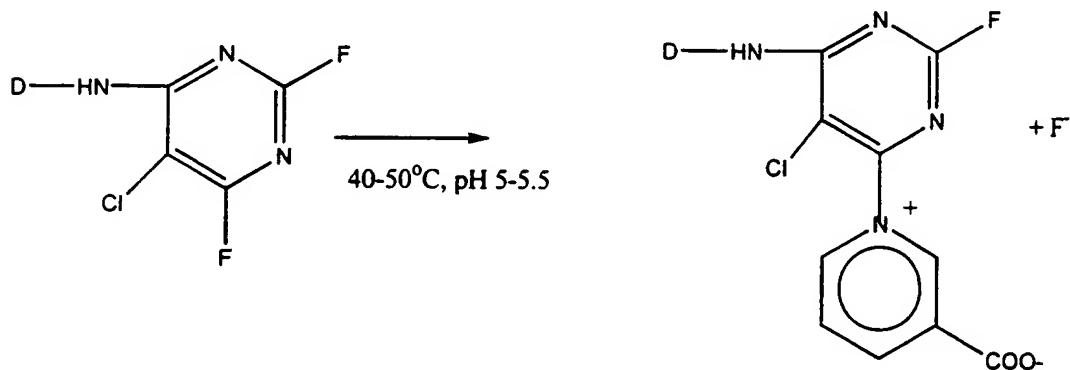


Diagram 15

In the reaction scheme D is a chromophore and varies depending on which starting dye is used. In the present example Drimarene Brill Red 4-KBL is used as the starting material. However any suitable pyrimidine containing dye can be used as a starting material including any Drimalan F dye, any Drimarene R dye and any Drimarene K dye commercially available from Clariant.

Synthesis of 5-chloro-4-nicotinyl-2-fluoro pyrimidine dye

0.1 moles of pure Drimarene Brill Red K-4BL dye in water are introduced into a flask. 0.1 mole of nicotinic acid is then added dropwise to the reaction mixture under stirring,
5 from a dripping funnel. The total addition time is 1-1.5 hours. The pH of the reaction system is maintained at pH 5-5.5 and the temperature of the reaction system 40-45°C, throughout the addition of nicotinic acid.

The reaction is then allowed to proceed at 40-45°C and pH 5-5.5 (which is corrected
10 using sodium carbonate and HCl) for 3-4 hours. The end-of-reaction point for this part of the synthesis is indicated by the pH of the reaction system remaining constant for more than 5 minutes. At this point, the 5-chloro-4-nicotinyl-2-fluoro pyrimidine dye is obtained. Using 6N HCl, the pH of the system is then reduced to below pH 2, to terminate the reaction. KCl (\cong 35% of the total solution) is then added to the reaction
15 mixture in order to precipitate the dye. Filtration using Whatman filter paper follows. The precipitate is then washed with acetone 4-5 time (\cong 50ml of acetone is used each time) to obtain the 5-chloro-4-nicotinyl-2-fluoro pyrimidine dye.

The compounds prepared according to Examples 1 to 15 all have high Fixation Values
20 on cotton fabrics (>95% as measured by the Fixation Value Technical Test Method described hereinabove).

In addition, the compounds prepared according to Examples 1 to 15 all have high Efficiency Values (T) on cotton fabrics (>90%) as calculated using the Fixation Values
25 and Exhaustion Values obtained from the Fixation Value and Exhaustion Value Technical Test Methods described hereinabove.

In addition, the compounds herein have high Exhaustion Values (E), and show significant improvements in terms of reducing spent dyestuff in effluent, increasing dye
30 affinity to the substrate, increasing the dye-substrate covalent bonding, increasing the ability to dye substrates at room temperature, decreasing the amount of dye that is removed during the post dyeing "soaping off process" and therefore simplifying the post dyeing "soaping off process" traditionally associated with dyeing cotton with fibre reactive dyes and reduction of staining of adjacent white fabrics. In addition, the
35 compounds prepared above provide more intense dyeings and require less levels of salt for dyeing cotton substrates. These advantages can be demonstrated by the following Examples 16 and 17.

Example 16

5 All dye compounds prepared according to Examples 1 to 15 can be used to dye cotton using the dyeing procedures detailed below. After the cotton dyeing procedure has been carried out a soaping-off process can also be carried out on the cotton fibre.

Cotton dyeing procedure

10 An aqueous dye solution is prepared containing a dye compound according to any of Examples 1 to 15. The dye solution contains 1.2% on mass of fibre of dye, 80g/L Na₂SO₄ and 5% on mass of fibre of sodium acetate. The cotton fabrics are soaked in water and then the cotton fabrics are dyed in the above dye-bath at pH 7 at 25 °C for 30 minutes. The dyed cotton fabric is then fixed in the dye-bath at pH 11.5 with addition
15 of 30g/L of sodium formate and 5g/L Na₂CO₃ and dyeing continued at 25°C for 30 minutes. The dyed fabric is rinsed with water.

In the above dyeing procedure the dye bath for each dye compound is almost totally exhausted, indicating that the compounds prepared according to Examples 1 to 15 each
20 have a high Exhaustion Value.

Soaping-off process

A soaping off process can then be carried out by washing the dyed fabrics with an
25 aqueous solution of Sandozine NIE (2g/L) at 100°C for 30 minutes.

In the above soaping-off process hardly any colour was removed from the fabric indicating that the compounds prepared according to Examples 1 to 15 each have a high degree of dye -fibre covalent bonding and a high Fixation Value.
30

Co3 (International Standards Organisation) Wash Fastness Test

The dyed fabrics are washed with an aqueous solution containing ECE Reference Detergent (5g/ml) and sodium carbonate (2g/ml) at 60°C for 30 minutes.
35

In the above wash fastness test, no noticeable colour was removed from the cotton fibre and no staining of the white adjacent fibres occurred (using Multiple Fibre adjacent strip supplied by SDC Bradford).

5 Example 17

All dye compounds prepared according to Examples 1 to 15 can be used to dye nylon or wool using the dyeing procedures detailed below. After the nylon/wool dyeing procedure has been carried out a wash-test procedure can be carried out on the dyed fabric to test the wash-fastness of the dye compounds.

Wool/Nylon Dyeing Procedure

The wool/nylon fabric is soaked in a 2% Alcopol-O (40% w/w sodium-d-
isooctylsulphate succinate -commercially available from Allied Colloids) solution. The fabric is then dyed for 1 hour at 100°C and pH 3.5 in a dye-bath containing the following compositions: 1.2% on mass of fibre of dye prepared according to any of Examples 1 to 15, 5% on mass of fibre of sodium acetate, 1% Albegal B (commercially available from Ciba Geigy). The dyed wool/nylon fabric was then rinsed with water.

In the above procedure intense dyeings are provided for each of the compounds prepared according to Examples 1 to 15.

Co2 (ISO) Wash Fastness Test Procedure for Wool/Nylon Fabrics

The dyed wool/nylon fabric is washed in an aqueous solution containing 5g/L of ECE Reference Detergent (commercially available from Society of Dyers and Colourists, Bradford, UK) at 50°C for 45 minutes.

In the above wash fastness test, no noticeable colour was removed from the wool fibre and no staining of the white adjacent fibres occurred ((using Multiple Fibre adjacent strip supplied by SDC Bradford).

WHAT IS CLAIMED IS:

- 5 1. Reactive dye having a Fixation Value (F) on cellulosic substrates of 95% or greater as measured by the Fixation Value Technical Test Method (at 2:1 standard depth).
2. Reactive dye according to Claim 1 wherein the Fixation Value is 97% or greater.
- 10 3. Reactive dye according to Claim 1 or 2 wherein the Fixation Value is 99% or greater.
4. Reactive dye according to any of Claims 1 to 3 having an Exhaustion Value (E) of 95% or greater as measured by the Exhaustion Value Technical Test Method.
- 15 5. Reactive dye according to Claim 4 wherein the Exhaustion Value is 90% or greater.
- 20 6. Reactive dye according to Claim 4 or 5 wherein the Exhaustion Value is 95% or greater.
7. Reactive dye according to any of Claims 4 to 6 wherein the Exhaustion Value is 97% or greater.
- 25 8. Reactive dye according to any of Claims 4 to 7 wherein the Exhaustion Value is 99% or greater.
9. Reactive dye having a Efficiency Value (T) of about 86.5% or greater, preferably 90% or greater.
- 30 10. Reactive dye according to Claim 9 having an Efficiency Value (at 2:1 standard depth) of about 93% or greater.
- 35 11. Reactive dye according to Claim 9 or 10 having an Efficiency Value of about 95% or greater.

12. Reactive dye according to any of Claims 9 to 11 having an Efficiency Value of about 97% or greater.
- 5 13. Reactive dye according to any of Claims 9 to 12 having an Efficiency Value of about 99% or greater.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/07294

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09B62/02 C09B62/503 C09B62/20 C09B62/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>JP 63 006181 A (NIPPON KAYAKU CO., LTD.) 12 January 1988 (1988-01-12) see page 5 formula (16); Table, compounds 1,3,4,5 & CHEMICAL ABSTRACTS, vol. 109, no. 8, 22 August 1988 (1988-08-22) Columbus, Ohio, US; abstract no. 56514g, T. SHIRASAKI ET AL.: "One-step one bath dyeing..." page 88; abstract & DATABASE WPI Section Ch, Week 8807 Derwent Publications Ltd., London, GB; Class A60, AN 88-047426 abstract</p> <p style="text-align: center;">---</p> <p style="text-align: center;">-/--</p>	1-13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 July 1999

Date of mailing of the international search report

01.09.99

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Ginoux, C

INTERNATIONAL SEARCH REPORT

In ternational Application No
PCT/US 99/07294

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 855 411 A (THOMPSON GLENN A ET AL) 8 August 1989 (1989-08-08) column 2, line 62 - column 3, line 3; claims; examples; table 2 ----	1-13
A	LEHR F: "SYNTHESIS AND APPLICATION OF REACTIVE DYES WITH HETEROCYCLIC REACTIVE SYSTEMS" DYES AND PIGMENTS, vol. 14, no. 4, 1 January 1990 (1990-01-01), pages 239-263, XP000176926 cited in the application see compounds 33,36,38,49; scheme 8; paragraph 3.1 ----	1-13
A	WO 96 02593 A (SANDOZ LTD ;SANDOZ AG (DE); SANDOZ AG (AT); LEHR FRIEDRICH (DE)) 1 February 1996 (1996-02-01) page 7, paragraph 3; examples ----	1-13
A	EP 0 418 623 A (BAYER AG) 27 March 1991 (1991-03-27) page 3, line 22 - line 25; claims ----	1-13
A	EP 0 260 806 A (ICI PLC) 23 March 1988 (1988-03-23) page 3, line 36 - line 38; claims ----	1-13
A	DE 14 44 295 A (SANDOZ AG) 24 October 1968 (1968-10-24) claims ----	1-13
A	EP 0 735 107 A (CIBA GEIGY AG) 2 October 1996 (1996-10-02) cited in the application examples ----	1-13
A	US 3 116 275 A (G.A.GAMLEN ET AL.) 31 December 1963 (1963-12-31) column 5, line 20 - line 23; claim ----	1-13
A	JP 60 208367 A (SUMITOMO CHEMICAL CO., LTD.) 19 October 1985 (1985-10-19) examples 1,5 & CHEMICAL ABSTRACTS, vol. 104, no. 26, 30 June 1986 (1986-06-30) Columbus, Ohio, US; abstract no. 226326, T.MIYAMOTO ET AL.: "dyeing and printing of fibrous materials..." page 77; abstract -----	1-13

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 99/ 07294

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-13
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
See further information sheet
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claims 1-13 relate to a compound defined by reference to a desirable characteristic or property, namely its Fixation, Exhaustion and/or Efficiency value.

The claims cover all compounds having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such compounds. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the compound by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the compounds prepared in examples 1-15

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

In: ational Application No

PCT/US 99/07294

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 63006181	A	12-01-1988	NONE	
US 4855411	A	08-08-1989	NONE	
WO 9602593	A	01-02-1996	DE 4425222 A	18-01-1996
			DE 4435380 A	11-04-1996
			BR 9508283 A	23-12-1997
			CN 1152930 A	25-06-1997
			EP 0772652 A	14-05-1997
			JP 10504330 T	28-04-1998
			TR 960059 A	21-06-1996
			US 5747657 A	05-05-1998
EP 0418623	A	27-03-1991	DE 3930996 A	28-03-1991
EP 0260806	A	23-03-1988	DE 3778101 A	14-05-1992
			JP 63075191 A	05-04-1988
			US 4881942 A	21-11-1989
DE 1444295	A	24-10-1968	DE 1619636 A	13-05-1971
EP 0735107	A	02-10-1996	DE 59108779 D	21-08-1997
			EP 0478503 A	01-04-1992
			EP 0735113 A	02-10-1996
			ES 2106070 T	01-11-1997
			HK 1001093 A	22-05-1998
			JP 4258674 A	14-09-1992
			US 5451665 A	19-09-1995
			US 5612463 A	18-03-1997
			US 5232462 A	03-08-1993
			US 5735911 A	07-04-1998
			US 5892006 A	06-04-1999
US 3116275	A	31-12-1963	DE 1209544 B	
			DE 1419859 A	02-10-1969
			GB 927772 A	
			GB 937182 A	
			US 3116103 A	31-12-1963
JP 60208367	A	19-10-1985	JP 1850443 C	21-06-1994
			JP 5062151 B	07-09-1993

THIS PAGE BLANK (USPTO)